University of Calgary

Natural Gas Processing Principles and Technology - Part I

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Purpose of this Document

1. To study the physical, chemical and engineering principles used in the handling of natural gas, substitute natural gas, their associated liquids, and the other compounds obtained from them.
2. To apply these principles to actual design and operating problems.

Preface

The gas processing industry in the past 25 years has developed extensively. Many different qualities of gas have been discovered and are being processed. Many different processing schemes are used to accomplish the same ends. This book tries to outline the major ways that this is being done, and to make the reader aware of the main areas of technology that are considered in gas processing and handling.

This book is intended for practising engineers of all disciplines as a guide for them in the gas processing industry as gas engineers come from all branches of engineering.

At the end of most chapters, typical problems that might be encountered in industry are given. As these are practical problems, more than the principles of the particular chapter have to be used to solve the problems.

The Gas Processors Suppliers Association Engineering Data Book[1] has been referred to extensively for data and other material as it is the basic reference book for the industry.

This book has been developed from the lecture notes developed by the author for a course given by him at the University of Calgary in the Department of Chemical Engineering over the past 24 years, and at other centres in both North America and Europe. During that period, several people have lectured in various sections of the course and have helped in the preparation of the text. These are, with the address when they participated in the course or their present address are as follows:

Dr. N. Anderson, Kilborn Engineering, Toronto, Ontario

Dr. K. Aziz, Stanford University, Palo Alto, California

Mr. E. Berlie, Western Research & Development, Calgary, Alberta

Dr. A. Chakma, University of Calgary, Calgary, Alberta

Dr. P.R. Bishnoi, University of Calgary, Calgary, Alberta

Dr. K. Goddard, Chevron Standard, Calgary, Alberta

Dr. G.A. Gregory, Neotechnology Consultants Ltd., Calgary, Alberta

Mr. G.E. Handwerk, Consultant, Denver, Colorado

Dr. R.A. Heidemann, University of Calgary, Calgary, Alberta

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[1] Published by the Gas Processors Suppliers Association and the Gas Processors Association, Tulsa, Oklahoma. Latest edition is the 10th edition which is published in English Units only. Page No.'s in the text refer to the Metric edition or the 9th English edition unless otherwise noted.

Mr. G. Kinsep, SKM Consulting, Calgary, Alberta
Mr. M.A. Kyllo, Ralph M. Parsons Company Ltd., London, England
Dr. D. Leahey, Western Research, Calgary, Alberta
Mr. J. Lore, Lore & Associates, Calgary, Alberta
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Mr. K.C. Milne, SKM Consulting, Calgary, Alberta
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Mr. H.G. Paskell, Western Research, Calgary, Alberta
Dr. D.B. Robinson, University of Alberta, Edmonton, Alberta
Mr. J. Same, Western Research, Calgary, Alberta
Dr. W.Y. Svrcek, University of Calgary, Calgary, Alberta
Dr. E.L. Tollefson, University of Calgary, Calgary, Alberta
Mr. E. Wichert, Petro Canada, Calgary, Alberta

Also, as the notes are based on the author's more than 30 years in the gas processing industry, he wishes to acknowledge the many persons not already acknowledged who contributed data and suggestions incorporate in the book.

The more recent revisions have been made to bring the notes up—to—date and to show both metric units and English units whenever appropriate. The problem of using metric units is that the source of much of the data is the 9th edition of GPSA Metric Data book, which is based on 1972 data. There is now available a 10th edition of this book which was published in 1987 that gives English units only. This is a much more complete reference book and as such will be used extensively in class.

1.0 Introduction

- Course objective, definition of terms, summary of Different fields touched on, etc.
- Typical gas analysis.
- Pipeline gas specifications and by-product specifications.
- The chemical composition of natural gas and the effect of these chemicals.
- Typical definitions used in natural gas processing.
- Simplified flow scheme of handling natural gas.

1.1 Natural Gas

Natural gas is defined as gas obtained from a natural underground reservoir. It generally contains a large quantity of methane along with heavier hydrocarbons such as ethane, propane, isobutane, normal butane, etc. Also, in the raw state it often contains a considerable amount of non— hydrocarbons, such as nitrogen, hydrogen suiphide and carbon dioxide. There are some traces of such compounds as helium, carbonyl sulphide and various n~rcaptans. It is also generally saturated with water. Table 1.1 below gives some examples of the analysis of various types of gas.

Table 1.1: Typical Raw Gas Composition

Geological Era	Mesozoic (Baldonnel) Mole %	Paleozoic (Kaybob South) Mole %	Solution Gas Mole %
N_2	0.32	0.94	2.45
H_2S	4.37	17.89	0.00
CO_2	2.41	3.49	0.11
Methane	85.34	56.53	91.94
Ethane	4.50	7.69	13.85
Propane	1.50	3.38	7.30
Isobutane	0.25	0.87	1.06
n-Butane	0.48	1.73	2.15
Isopentane	0.15	0.71	0.36
n-Pentane	0.21	0.76	0.48
Hexane	0.47+	1.48	0.18
Heptane plus	-	4.53	0.12

1.2 Why Process Natural Gas?

Gas that is sold for commercial use is quite different in composition to the gas given in Table 1.1. A typical composition of a gas that is sold directly as an industrial fuel is given in Table 1.2.

Table 1.2: Typical Pipeline Gas Composition

	From a Field Plant Mole %	From a Straddle Plant Mole %
N_2	0.30	0.35
C_1	91.63	98.60
C_2	5.72	1.05
C_3	1.63	____
iC_4	0.29	____
nC_4	0.31	____
iC_5	0.12	____

The gas that is sold is not specified by chemical composition, but rather by a series of specific properties that have to be met. These are given in Table 1.3 and Table 1.4. To change the raw gas in the reservoir, which is at pressures from 600 psig (4000 kPa) or lower to 5000 psig (35000 kPa) or higher and is generally saturated with water vapour, to a gas of the composition of Table 1.2 it can be seen that the gases of the compositions given in Table 1.1 will need considerable processing.

All the acid gas compounds, H_2S and CO_2 , must be removed, and if it is economical, or required for environmental reasons the H_2S should be converted to elemental sulphur. Also, all the free liquids, both hydrocarbon and water, have to be removed. In fact, generally all the hydrocarbons heavier than pentanes are removed as well as considerable amounts of propane and butane. The removal of these compounds requires an understanding of the laws of fluid flow, distillation, heat transfer, etc. These subjects, along with others, will be discussed later in the book.

1.3 Chemical Composition of Natural Gas

Natural gas is a complex mixture of hydrocarbon and non-hydrocarbon constituents and exists as a gas under atmospheric conditions. Virtually hundreds of different compounds may be present in natural gas in varying amounts. Even two wells producing from the same reservoir may produce gases of different composition as the reservoir is depleted.

The complex nature of natural gas is exemplified by the American Petroleum Institute's Research Project 6, which determined the individual constituents of a naturally occurring petroleum hydrocarbon mixture. Using a sample of Ponca City Field petroleum, this project isolated 172 compounds. Natural gases may have a similar complexity. Fortunately, however, the major components in most natural gases are paraffin hydrocarbons with smaller amounts — usually only traces - of olefin hydrocarbons, naphthenic hydrocarbons, mercaptans, and non-hydrocarbon compounds.

The components of natural gas are either aliphatic (chain) or cyclic (ring) hydrocarbons. Their structures are as follows.

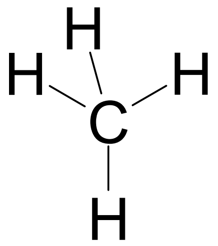
Aliphatic or Chain Hydrocarbons

Aliphatic hydrocarbons occur in two forms: paraffin hydrocarbons and olefin hydrocarbons. The most common are saturated hydrocarbons.

- CH_4 - Methane (predominant)
- C_2H_6 - Ethane
- C_3H_8 - Propane
- C_4H_{10} - Butane

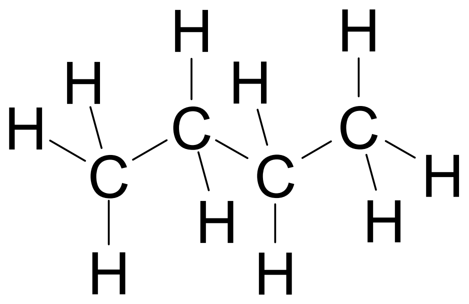
- C_5H_{12} - Pentane
- C_6H_{14} - Hexane
- C_7H_{16} – Heptane

The structural formula for methane is

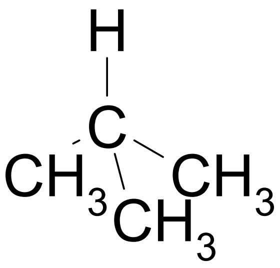


Isomers

Isomers are compounds having the same composition and molecular weight but different properties due to a different structural arrangement. The structural formulae for butane isomers are as follows:



Normal butane



Isobutane

Olefin hydrocarbons

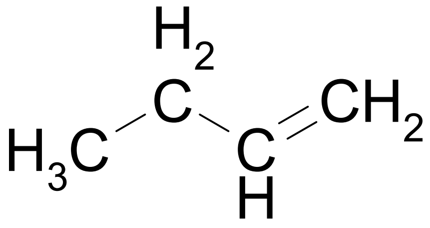
Olefin hydrocarbons have the general formula of C_nH_{2n} and are classed as unsaturated hydrocarbons. They usually occur only in traces.

C_2H_4 - Ethene

C_3H_6 - Propene

C_4H_8 - Butene

The structural formula for butene is

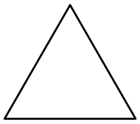


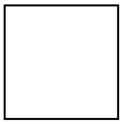
Cyclic or Ring Hydrocarbons

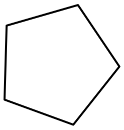
Cyclic hydrocarbons also occur in traces most of the time. They are of two kinds: naphthenic, and aromatic, hydrocarbons. For simplicity, only the ring structures will be shown.

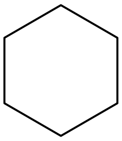
Naphthenic hydrocarbons

Naphthenic hydrocarbons are saturated cyclic hydrocarbons with the general formula of C_nH_{2n}


Cyclopropane

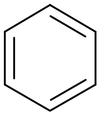

Cyclobutane

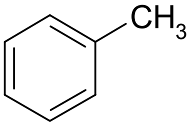

Cyclopentane


Cyclohexane

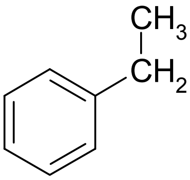
Aromatic hydrocarbons

Aromatic hydrocarbons are unsaturated cyclic hydrocarbons classified by the number of six—carbon rings in the molecule. The structures of benzene, toluene, and ethyl benzene are as follows:


Benzene

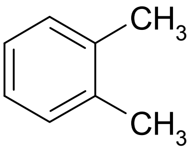


Toluene (Methyl benzene)

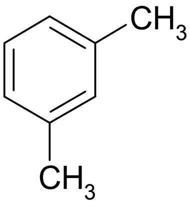


Ethyl benzene

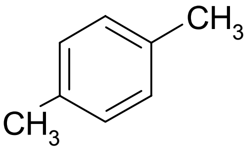
Structures of more complex aromatics such as ***xylenes*** in which two or more methyl groups or side chains are attached to the benzene ring are shown below:



Orthoxylene



Metaxylene



Paraxylene

Nonhydrocarbon Components

Some non-hydrocarbon components of natural gas are as follows:

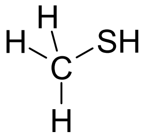
Nitrogen	N_2
Carbon dioxide	CO_2
Hydrogen sulfide	H_2S
Helium	He
Water vapor	H_20

Carbonyl sulfide	COS
Carbon disulfide	CS_2
Sulfur	S
Mercaptans	*RSH

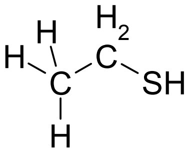
Note: R represents an alkyl group

Methyl Mercaptan and Ethyl Mercaptan

Methyl mercaptan and ethyl mercaptan are the two mercaptan compounds most commonly found in natural gas. Their structures are as follows:



Methyl mercaptan



Ethyl mercaptan

The effect of the various compounds on natural gas will now be discussed.

Nitrogen (N_2)

This compound is quite inert and does not contribute to the gas in any way. It should be noted that gases with high N_2 content often have high helium content.

Hydrogen Sulphide (H_2S)

This compound is the cause of the sourness in natural gas. It is one of the most dangerous of industrial gases. For example, if a person is exposed to a concentration of 0.06% in air for two minutes, it will probably result in his death. Thus, H_2S has to be removed from the raw gas. This is done primarily by the process of sweetening. The H_2S content of gas is reduced to less than either 0.25 (.4 ppm) or 1 grain (16 ppm) per 100 CF of gas, depending on the pipeline the gas is being sold to. Thus, 1 grain pipeline gas contains less than 0.0016% H_2S. The actual metric specifications are 6 mg/in or 23 mg/m^3

Carbon Dioxide (CO_2)

This compound is an acid gas like H_2S, but it is not nearly so undesirable. It does not support combustion and thus does not contribute to the gas. The normal maximum acceptable concentration in pipeline gas is 2%. Often gases of higher contents are accepted from small fields as it does not pay to remove the CO_2 if only it is present. The sweetening process also is used for the removal of CO_2

Carbonyl Sulphide (COS)

This is a compound that often appears in raw gases with high concentration of H_2S in them. It is generally reported in grains per 100 CF (or in ppm or mg/m^3). It has the undesirable property of forming nonregenerable compounds with one of the most commonly used sweetening agents, monoethanol amine. This causes increased chemical consumption of this agent. Other sweetening agents such as "diethanol amine", "sulphinol", etc., can be used to absorb it. The COS is generally broken down in the regeneration step with these agents.

Methane (CH_4 or C_1)

This is the prime compound in natural gas.

Ethane (C_2H_6 or C_2)

This compound occurs as the second largest component of all natural gases. It has a considerably higher gross heating value than methane (1769 BTU's/SCF versus 1010 BTU's/SCF 3 3 of gas or 66.0 MJ/m versus 37.7 MJ/m).

Propane (C_3H_8 or C_3)

This compound is a significant part of pipeline gas. However, if there is much present in the raw gas, say 2.0% or greater, then it is generally more economical to absorb it and recover it as a liquid and sell it as a liquid fuel.

Isobutane ($iC_1.\sim H_{10}$ or iC_4)

This compound is normally extracted as liquid. It is used as a component in the manufacture of high octane gasoline (alkylate).

n Butane (nC_4H_{10} or nC_4)

This compound is normally extracted as a liquid. It is generally used as a blending agent in motor gasoline.

Pentanes and Heavier (C_5H_{12} or C_5 or heavier)

These compounds appear in pipeline gas only in small quantities. They are mostly in the form of liquids when entering the processing

plant. They are separated and are the primary compound in condensate.

Mercaptans (CH_3SH - methyl mercaptan or C_2H_5SH - ethyl mercaptan)

These are very foul smelling compounds that, in very small quantities can be used as gas odorants, but in larger quantities make the gas offensive to certain consuming areas.

1.4 Further Discussions on Pipeline Gas Specifications

Table 1.3 lists the various specifications used for gas purchased in Western Canada. In the previous section, the reasons for some of the specifications are given. However, a review of the other is necessary.

Table 1.3: Typical Pipeline Gas Specifications

Specification Item	Trans Canada	Alberta & Southern	Westcoest For US Use	Westcoast For BC Use	Canadian - Western
Minimum Heating Value Btu/SCF	950	975	1000	1000	950
Hydrocarbon Dewpoint, F	15 @ 800 psia	15 @ 800 psia	Free of Liquids	Free of Liquids.	15 @ 500 psia
Water Content	4	4	4	4	Equivalent to

Lb/MMSCF					dewpoint
Hydrogen Sulphide Grains per 100 CF	1	0.25	0.25	1	1
Mercaptans Grains per 100 CF	No spec	0.20	5.0	No spec	No spec
Total Sulphur Grains per 100 CF	20	1.0	20	20	10
Carbon Dioxide, mole%	2	2	1	No spec	No spec
Oxygen Content, mole %	No spec	0.4	0.2	1	No spec
Delivery Temperature, F	120	120	No spec.	No spec	120
Delivery Pressure, psig max.	900	900	varies	varies	500

Table 1.4: General Metric Specifications

Specification Minimum	Traditional Value	Rationalized SI Specifications
Heating Value	950 BTU's/scf	34.5 MJ/m^3
Hydrocarbon Dew Point	15°F at 800 psia	—10°C at 5500 kPa
Water Content	4 lbs/MMSCF	65 mg/m^3
H_2S Content	1/4 grain/100CF	6 mg/m^3
Total Sulfur Content	1 grain/100CF	23 mg/m^3

1.4.1 Special specifications

Equation 1-1

$$Wobbe\ No. = \frac{Gross\ Heavy\ Value\ in\ BTU/SCF}{\sqrt{Specific\ Gravity}}$$

This is a measure of the burning qualities of the gas. Gases mixed together should have Wobbe number within 10%.

Heating Value

This is necessary so that the consumer can properly set his firing equipment. Most pipeline companies give a bonus for increased BTU content above 1000/SCF (on gross basis as explained in Chapter 2).

Hydrocarbon Dewpoint

This specification is necessary to prevent the condensation of liquid hydrocarbons in pipelines transmitting gas to markets or in the lines feeding consumers. When a deep cut extraction plant straddles a pipeline some distance down the line, this specification is not too important as long as free liquids do not form and remain in the transmission lines.

Water Content

This specification is necessary to prevent condensation of liquid water in the pipelines as the presence of free water is conducive to the formation of hydrates. The specification of 14 lbs of water/MMSCF is equivalent to a dew point of +18°F (-9°C). As the lowest buried pipeline temperature that has been measured in operating conditions is +25°F C~l4°C) this specification gives a reasonable degree of safety.

H_2S Content

This specification is explained in the previous section.

Mercaptan Content

This specification is explained in the previous section. It is particularly applicable for gas going to California as the customers there are used to very sweet smelling gas.

Total Sulphur

This specification is also set for the same reason as the mercaptan specification; that is, to control the foul smelling compounds. These can be, besides mercaptans, thiophenes and disulphides. Also, sulphur compounds can be a catalyst poison in some reactions involving natural gas.

CO_2 Content

This was discussed in the previous section.

O_2 Content

This is not an important specification as 0 is not normally present. It is a hold-over from manufactured gas specifications.

Delivery Temperature

This is set, sometimes, to have consistent metering and also to protect pipeline coatings.

Delivery Pressure

This is set so that the pipeline company can properly design their system. The higher, the better for the pipeline company.

1.5 Definitions

Please also see GPA Publication 1167 -77 "Glossary Definition of Words and Terms Used in the Gas Processing Industry". This is now included in Chapter 1 of the English Unit version of the GPSA Engineering Data Book.

It is desirable to define several of the terms that will be used in the book. Some of the main ones are as follows:

Raw Gas (natural gas)	Untreated gas from/or in the reservoir

Pipeline gas or Residue Gas or Sales Gas	Gas that has the quality to be used as a domestic or industrial fuel. It meets the specifications set by a pipeline transmission company, and/or a distributing company
Sour Gas	Gas that contains more than 1 grain of H_2S/l00 SCF. Generally much more than this.
Sweet Gas'	Gas in which the hydrogen sulphide content is less than 1 grain per 100 SCF.
Wet Gas	Gas that contains more than 0.1 gallons (U.S.) of condensate per 1000 CF of gas.
Dry Gas	Gas that contains less than 0.1 gallons of condensate per 1000 CF of gas.
g.p.m. for a gas	Gallons of liquid per 1000 CF of gas. This can be US or Imperial Gallons.
Rich Gas	Gas containing a lot of compounds heavier than ethane, about 0.7 US gallons of C_3+ per 1000 CF of feed to an absorption unit.
Lean Gas	Gas containing very little propane and heavier – or the effluent gas from an absorption unit.
Pentanes +	The pentane and heavier fraction of hydrocarbon liquid.
Condensates	The hydrocarbon liquid fraction obtained from a gas stream containing essentially pentanes +.
Natural gasoline	A specification product of a certain vapour pressure. See GPSA data book for the various grades.
Lean Oil	Absorption oil sent to an absorber.
Rich Oil	Absorption oil containing absorber material. The effluent from an absorber.
Lean Solution	A stripped sweetening solution.
Rich Solution	A sweetening solution containing absorbed acid gases.

1.6 Calculations Involving Gas Composition

Often it is desirable to calculate certain figures regarding raw gas based on its chemical compositions. For example, let us calculate the long tons of sulphur/MMSCF, the pentanes+ BBls/MMSCF and propane+ in US gallons per MSCF for the gas given in Table 1.6

The pentanes plus content is determined by finding the US Gallons per 1000 CF from the table (sum of iC_5, nC_5, C_6+) and multiplying by 1000 and converting to BBls:

Equation 1-2

$$\frac{0.413\,(1000)}{42} = \frac{9.8BBls}{MMSCF}$$

Table 1.5: Gas Composition

Comp.	Mole %	US Gallon per mole	US Gallon per 1000 CF
N_2	0.69	4.16	--
H_2S	6.14	5.17	--
CO_2	1.00	6.38	--
C_l	82.15	6.40	--
C_2	6.30	10.12	--
C_3	1.84	10.42	0.504
iC_4	0.38	12.38	0.124
nC_4	0.50	11.93	0.156
iC_5	0.30	13.85	0.110

nC_5	0.20	13.71	0.072
$*C_{6+}$	0.50	17.46	0.231
		Total	**1.197**

* Assume to have properties of nC_7

The propane$^+$ content of the gas as is shown in the Table is 1.197 gallons per 1000 CF. The calculation of propane content alone is as follows:

$$=\frac{1.84}{100}\left(\frac{1000}{379}\right)(10.42)=0.54\,\frac{US\ Gallons}{1000\,CF}$$

The sulphur content is found as follows:

$$\frac{1.84}{100}\,\frac{10^6}{379}\,\frac{32}{2240}=\frac{2.32\,LT}{MMSCF}$$

The equivalent metric calculation is shown below.

For propane find the m^3 of C_3 liquid per 1000 m^3 of gas

$$\frac{1.84}{100}\,\frac{1000}{23.6}\,\frac{0.08684}{1000}=0.06770\quad cu.m.$$

(for liquid propane) thus must be divided by 1000 to get to moles. For sulphur content in tonnes (1000 kg) /1000 m of gas

$$\frac{6.14}{100}\,\frac{1000}{0.0236}\,\frac{32}{1000}\quad=\quad 0.08325$$

1.7 By-Products from Natural Gas

The by-products that are recovered from processing natural gas are generally propane, mixed butanes (sometimes this is split into iso and normal butane), condensate or pentanes plus, and sulphur.

Propane and Butanes: The use of propane and butanes were given in a previous section. The primary specifications for propane and butane are given in Tables 1.7 and 1.8.

Table 1.6: LPG Specifications[∇]

Item	Propane	Butane
Vapor Press. Max, psig at 100 F	208	70
Residue or butane content %	2	Not a spec.
95 % boiling point	Not a significant spec.	34°F

[∇] See Figure 15-50 in the GPSA Data Book for more complete Specs (or Fig. 2.4 English GPA Data Book).

Volatile suphur grains/IO0 CF	15.0	15.0
Dryness	by valve freeze test.	No free moisture.
Corrosive Compounds	Free from (#1 by copper strip)	Free from (#1 by copper strip)

"Valve Freeze" method of ASTM (Test D2713-81)

Table 1.7: LPG Specifications Metric Equivalents

Item	Propane	Butane
Vapour Press. Max kPa gauge at 37.8°C	1434	483
95% BP	--	2.2°C
Volatile sulphur mg/m^3 (15 grains)	343	343
Volatile sulphur mg/m^3 (10 grains)	229	229

In the HD-5 specification for propane, additional restrictions such as 10 grains of sulphur/100 CF, 5% maximum propylene (C3H6), 90% minimum C3 are added. In the winter time Canadian companies often use a higher vapour pressure specification than allowed by HD-5 because of the cold conditions.

Table 1.8: Required Characteristics of Liquefied Petroleum Gases

Item	Commercial Propane	Commercial Butane	Method of Test
Vapour pressure at 40°C, max kPa (gage)	1550	520	ISO 4256
Volatility			
C4 hydrocarbons, mol percent, max	7.5	--	ISO 7941
C5 hydrocarbons, mol percent, max	--	2.0	ISO 7941
C5 and heavier hydrocarbons, mol percent, max	0.1	--	ISO 7941
Unsaturates, mol percent	Report(3)	Report(3)	ISO 7941
Butadienes, mol percent, max	0.5	0.5	ISO 7941
Residual Matter mg/kg, max	50	50	(4)
Relative density, at 15°C, kg/m^3	Report	Report	ISO 3993(5)
Corrosiveness to Copper, max	1	1	ISO 6251
Sulfur, mg/kg, max	50	50	(6)
Hydrogen sulfide	pass	pass	(7)
Moisture content	pass	--	(8)
Free water content	--	None(9)	

Note to Table 1.8:

Certain national standards arA/or regulations may prescribe lower vapor pressure limits.

Vapor pressure may be calculated from compositional data. An ISO method is undek development. However, in case of dispute about the vapor pressure, ISO 4256 shall prevail.

Certain nattotial star4ards may prescribe a limitation on unsaturgtes.

A suitable ISO method is being investigated. Until an ISO method is available, th appended Shell Method Series 5145 1513-2 is recommended.

Relative density may be calculated from compositional data. An ISO method is undet development.

A suitable ISO method is bein; developed. Until an ISO method is available, test in accordance with a procedure that is technically equivalent to ASTM D-2784-BO (1983 Annual bc'ok of ASTM Standar"s, Section 5, page 699).

A suitable ISO method is being developed. Until an ISO mothod is available, test in accor4~nco with a procedure that is technically equivalent to ASTM D-2420-81 (.1983 Annual Book of ASTM Standards, Sect:ion 5, page 344).

Ethane

One of the present Canadian specification for ethane is

C_2	95 Mole % Min.
CO_2	2.0 Mole % Max.
C_1	2.0 Mole % Max.
C_3	2.0 Mole % Max.
H_2S	100 ppm Max.

Pentanes

Pentanes plus is normally just the heavier portion of the liquids recovered from a gas processing plant. Generally, a specification of 12-14 psia for a Reid Vapour Pressure has to be met, and often the quantity of butane is limited to 3% for full credit as pentanes + varies quite considerably both as to its distillation and as to its composition. A detailed discussion of the chemical composition of condensate is given in a paper by M. Gawlak[1].

Sulphur

Sulphur is generally recovered by burning the H_2S recovered from the regeneration of the sweetening solution with a controlled amount of air. The following equations show the reactions that normally occur:

$$H_2S \;+\; 1.5\,O_2 \;\rightarrow\; H_2O \;+\; SO_2$$

$$2\,H_2S \;+\; SO_2 \;\rightarrow\; 2\,H_2O \;+\; 3\,S$$

The specification for sulphur is 99.5% pure, yellow in colour, and with no arsenic or selenium present. Texas Gulf Sulphur have set up a colour specification that makes sure that less than 0.05% C is present if their specification is met. See **Error! Reference source not found.** for Sulphur Specs.

1.8 General Processing Schemes

The steps in processing a raw, sour, rich natural gas saturated with water are shown schematically in **Error! Reference source not found.**. The raw gas in the reservoir is assumed to be at 4000 psig (28,000 kpa) and 150^{0}F (65^{0}C). It is brought to the surface via the tubing in the well where it is reduced in pressure to the operating pressure of the gas gathering line (normally less than 1440 psig) (10,140 kpa). This is for the use of 600 psi ANSI fitting valves. Since the gas cools, when it is reduced in pressure, some of the water of saturation condenses out. This is conducive to hydrate formation. Similarly, as the gas is transmitted to the processing plant, if the distance is more than two miles, the gas will cool to ground temperatures of +25^{0}F (-4^{0}C) to 30^{0}F (-1^{0}C) and water will also condense out. This, of course, will be conducive to formation of hydrates which will plug the pipelines. Therefore, at the well site hydrate prevention processes have to be used. These are either the heating of the gas to keep it above its hydrate point or the dehydration of the gas to remove the water. The gas is then transmitted to the processing plant via a pipeline. The flow will be generally two phase.

Upon entering the plant, the gas enters a separator where the liquids are dropped out. The gas is then sent to a sweetening unit where the acid gases are removed; generally by a sweetening agent such as monoethanol amine (MEA), diethanol amine (DEA), sulphinol, and others. The gas leaving the sweetening unit is now sweet, but is still saturated with water vapour and still contains a considerable amount of heavy hydrocarbons.

Table 1.9: Sulphur Product Specifications

A sulphur product meeting the following specifications will normally satisfy the requirements of the major consumers of sulphur such as manufacturers of sulphuric acid, chemicals, fertilizers, etc.:

Purity	99.5% - 99.8% by weight (dry basis)
Acidity (as H_2SO_4)	Less than 0.05% by weight
Moisture	Nil to 1.0% by weight
Ash	Less than 0.1% by weight
Carbonaceous Matter	Less than 0.15% by weight
Arsenic, Tellurium, Selenium	Commercially Free[◊]
Colour	Bright yellow at ambient temperature.

Note: The colour of sulphur is an important property because it gives an immediate indication of product purity. The sulphur is a bright yellow if the impurity content is less than about 0.02% by weight. Small amounts of carbon (soot) change the bright yellow colour to dull yellow or green; "dark" sulphur in which the yellow colour has a shade of grey or brown usually contains 0.1% - 0.5% by weight of carbon. For sulphuric acid manufacturer, however, sulphur colour is usually less important than ash and heavy metal contents.

These both must be removed so that the water dewpoint and hydrocarbon dewpoint specifications can be met. This is done by several processes. For example, the gas may be chilled by refrigeration to below the dewpoint for both the water and the hydrocarbon so that the water and heavy hydrocarbon condense out. In this case, glycol is added to the gas stream at the beginning of the process to prevent hydrates or freezing. In another series of processes, the heavy hydrocarbons may be removed by absorption and the water removed by dehydration.

[◊] Contents of less than 0.25 ppmw of arsenic and 2.0 ppmw of Selenium and Tellurium are usually considered as 'Commercially Free'.

The liquid hydrocarbons from the separation facilities and from the hydrocarbon dewpoint control facilities are sent to fractionation facilities for the separating of the hydrocarbons into individual compounds.

The acid gas H_2S and CO_2 are sent to a sulphur recovery unit in which the H_2S is reacted with 0_2 from air to form elemental sulphur.

The recovery level of sulphur is set by governmental authorities. The CO_2 and SO_2 (that part of' the H_2S not converted to S) is rejected to the atmosphere.

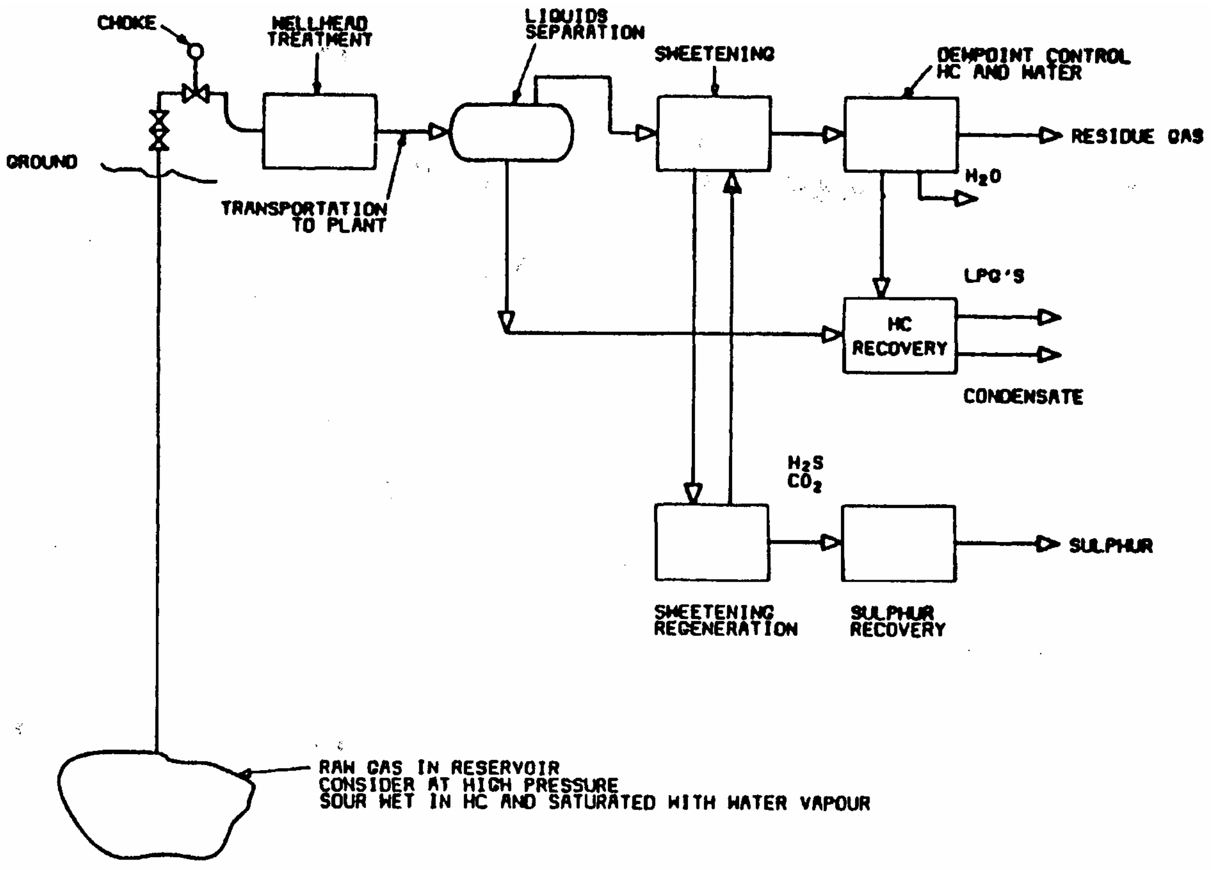


Figure 1.1: ***Overall Gas Processing Scheme***

References

1. M. Gawlak, Gas Processing/Canada, Sept./Oct. 1971, P. 26

Reading List

1. J.A. Richardson, R.F. Smith, and All. Younger, "Gas Processing in Canada During the Last 20 Years", Energy Processing Canada, Nov./Dec. 1979, P. 41.
2. Henningser, G., and D. Bergenson, "Natural Gas Composition and Productions" Energy Processing Canada, July/August 1974 P. 32.
3. Cannon, R., "Gas Processing Developments Set Stage for 1984 to be a Banner Year", Oil and Gas Journal, July 18, 1983.
4. "The Gas Processing Industry: Its function and Role in Energy Supplies", GPA 1985.
5. Stenson, F., "Waste to Wealth", Friesen 1985.

2.0 Physical Properties of Light Hydrocarbons and Other Associated Compounds

- Physical properties.
- Heating value.
- Critical properties.
- Equations of state.
- Compressibility factors for gases and other physical properties.
- Special effects of sour gas.

2.1 Introduction

The physical properties of the fluids we are dealing with in natural gas processing are of prime importance in the design of equipment and facilities to handle these fluids. Some of the important properties are:

1. Density and/or the compressibility of a gas
2. Density of a liquid
3. Specific heats
4. Enthalpies
5. Entropies
6. Free energies
7. Heat of combustion
8. Heat of reaction
9. Viscosities
10. Thermal conductivities
11. Surface tension

There are available for individual compounds considerable data on the effect of temperature and pressure on the various properties given above. For example the GPSA Data Book on Fig. 16-1, and on other pages, give a lot of data for individual compounds and some data for mixtures. Also, Maxwell[6] and Katz[7] are good references. A book providing the thermal properties of hydrocarbon has been published by Canjar and Manning[16]. Another good reference is by C.J. Sciance, C.J. Clover, and C.M. Shepvich.[8]

From the above and from other data we are primarily interested in predicting the properties of mixtures of pure compounds at varying temperature, pressures and compositions.

2.2 Densities

Let's start by finding the densities of gases. To do this we must calculate the compressibility of gases. Let us review some basic laws. First we have the Ideal Gas Law:

Equation 2-1

$$PV = RT$$

for 1 mole of gas. This law is a combination of the old Boyle's Law and Charles' Law. It assumes that the molecules occupy no space and have no attractive forces. It applies at low pressures and when compounds are a long way from their condensing temperatures.

Another law that we use considerably is a form of Dalton's Law or the Ideal Solution Law. That is, the sum of mole fraction of each compound present multiplied by the physical property of each pure compound at the conditions of the system gives the value of the physical property at the condition of the system. This law is used considerably.

The Ideal Gas Law is not too applicable to light hydrocarbons and their associated fluids. It is necessary to use more refined equations. There are two general methods of correcting the Ideal Gas Law equation:

1. By using an expanded equation of state
2. By using a correction factor in the equation PV = RT

   ie.

Equation 2-2

$$PV = ZRT$$

This method is used a great deal in light hydrocarbon work. However, equations of state are coming more into use because of the availability of computers.

2.2.1 Equations of State

One of the first and most famous was developed by Van der Waals in 1873. This equation is:

Equation 2-3

$$\left(P + \frac{a}{v^2}\right)(V - b) = RT$$

where "a" is the attractive force between the molecules and "b" is the volume occupied by the molecules. For each compound a different value of "a" and "b" has been developed. The Chemical Engineer 's Handbook gives data for the contents.

Another famous equation is the Beattie Bridgeman equation developed in 1927. The equation is:

Equation 2-4

$$P = \frac{RT}{V^2}\left(1 - \frac{c}{VT^3}\right)V + B_0\left(1 - \frac{b}{V}\right) - \frac{A_0}{V^2}\left(1 - \frac{a}{V}\right)$$

where A_0, B_0, a, b, and c are constants for a particular gas. This applies to pure compounds and mixtures of gases of similar chemical species. It cannot be used for liquid vapour phase behaviour.

This equation is the basis for the virial equation of state of which the one discussed next is a prime example.

These two previously mentioned equations are not used much now but rather the following equations are used.

An equation that has been useful in the prediction of PVT in two phase regions is the Benedict-Webb-Rubin equation (BWR), developed in 1940, and modified by Starling in 1970, [1,2](BWRS)

Equation 2-5

$$P = RT\rho + \left(B_0RT - A - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4} \right)\rho^2 + \left(bRT - a - \frac{d}{T} \right)\rho^3 + \left(a + \frac{d}{T} \right)\alpha\rho^6 + \frac{c\rho^3}{T^2}\left(1 + \chi\rho^2\right)\exp\left(-\chi\rho^2\right)$$

where: B_O, A_O, C_O, D_O, E_O, b, a, α, c, d, γ are constants for a particular compound. For example, the constants for light hydrocarbons, N2, and CO_2 as determined by Hopke & Lin[3] are given in **Error! Reference source not found.**. The units used in this table are:

Pressure = psia

Density = (lbmoles) (cu. ft.)

Temperature = °Rankine

R = 10.7335 (psia cu ft) (lbmole °R)

To handle mixtures the following set of equations are used for each constant according to Hopke & Lin.

Table 2.1: The Optimal BWRS Parameters

	CH_4	C_2H_6	C_3H_8	$I\text{-}C_4H_{10}$	$N\text{-}C_4H_{10}$	$I\text{-}C_5H_{12}$	$N\text{-}C_5H_{12}$	N_2	CO_2
B_O	0.69663	0.940341	1.15091	1.41699	1.38780	1.61871	1.54342	0.686293	0.473428
$A_O/10^4$	0.703241	1.50851	2.20325	3.01020	3.12799	3.93334	3.95713	0.424533	0.762197
$C_O/10^8$	3.31272	26.0615	75.3232	137.356	159.698	257.683	284.646	0.974169	20.8025
γ	1.39930	3.04151	5.50136	8.82944	9.00761	12.7727	13.0384	1.19172	1.26588
b	0.861307	2.69564	6.36610	10.6254	11.2723	16.7246	18.8648	0.559419	9.976469
$a/10^3$	2.75239	17.3349	55.8356	101.674	113.271	184.751	207.942	0.921051	6.05085
α	0.453145	1.03845	2.17606	4.37780	4.24116	7.10095	6.99803	0.48971	0.32038
$c/10^9$	0.508281	5.94592	23.3092	52.3431	62.8476	120.128	131.746	0.112862	2.41003
$D_O/10^{10}$	1.41063	20.7312	75.6999	160.026	195.633	349.884	412.701	0.362181	15.5050
$d/10^5$	0.684469	5.98254	18.744	40.6431	46.7125	84.3874	97.2323	0.282061	3.48824
$E_O/10^{11}$	1.26531	90.0981	437.431	1056.56	1381.81	2894.06	3518.30	0.327911	107.933

To handle mixtures the following set of equations are used for each constant according to Hopke & Lin.

Search Main Menu

Table 2.2: Mixing Rules – BWRS Equation

Equation 2-6

$$B_0 = \sum_i x_i \, B_{0i}$$

$$b^{1/3} = \sum_i x_i b_i^{1/3}$$

$$A_0 = \sum_i \sum_j \left(\frac{m_{ij}}{2} \right)^3 x_i x_j A_{0i}^{1/3} A_{0j}^{1/2}$$

$$a^{1/3} = \sum_i x_i a_i^{1/3}$$

$$C_0 = \sum_i \sum_j \left(\frac{m_{1j}}{2} \right)^3 x_i x_j C_{0i}^{1/2} C_{0j}^{1/2}$$

$$\alpha^{1/3} = \sum_i x_i \alpha_i^{1/3}$$

$$\chi^{1/2} = \sum_i x_i \chi_i^{1/2}$$

$$c^{1/3} = \sum_i x_i c_i^{1/3}$$

$$D_0 = \sum_i \sum_j \left(\frac{m_{ij}}{2} \right)^4 x_i x_j D_{0i}^{1/2} D_{0j}^{1/2}$$

$$d^{1/3} = \sum_i x_i d_i^{1/3}$$

where x_i. is the mole fraction of the "ith" component for the homogeneous phase under consideration, and parameters with subscript "i" refer to the "ith" pure component, m_{ij} is the interaction parameter between binary mixtures, and is equal to 2.0 for i = j. Another common interaction coefficient is k_{ij}; $m_{ij} = 2(l- k_{ij})$.

The values of m_{ij} between binaries of hydrocarbons, N_2, and $C0_2$, as determined by Hopke & Lin, are given in the following table.

Table 2.3: Optimal Interaction Parameters m_{ij}

	C1	C2	C3	I-C4	N-C4	I-C5	N-C5	Nitrogen	Carbon Dioxide
C1	2.000								
C2	1.999	2.000							
C3	1.998	2.011	2.000						
I-C4	1.997	1.998	1.999	2.000					
N-C4	1.997	1.998	1.999	2.000	2.000				
I-C5	1.996	1.997	1.998	1.999	1.999	2.000			
N-C5	1.996	1.997	1.998	1.999	1.999	2.002	2.000		
Nitrogen	1.954	1.926	1.913	1.883	1.883	1.921	1.921	2.000	
Carbon Dioxide	1.943	1.928	1.913	1.894	1.898	1.900	1.887	2.015	2.000

Another set of mixing rules also using interaction coefficients (k_{ij}) has been proposed by Bishnoi & Robinson[4]

This equation is used for predicting all PVT data and vapour liquid phase behaviour of inulticomponent mixtures. Another equation of state that has gained favour is the Redlich Kwong[19] equation which was published in 1949.

Equation 2-7

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}\,V(V+b)}$$

or Z, the compressibility factor as given in the other type of equation, can be expressed as follows:

Equation 2-8

$$Z = \frac{1}{1-h} - \frac{A^2}{B}\left(\frac{h}{1+h}\right)$$

Where

$$h = \frac{b}{V} = \frac{BP}{Z}$$

where a, b, or A, B are adjustable parameters of a particular gas and can be calculated from the gases critical properties.

$$A^2 = \frac{a}{R^2 T^{2.5}} \qquad B = \frac{b}{RT}$$

$$a = 0.4278\, T_C^{\,2.5}\, \frac{R^2}{P_C}$$

$$b = 0.0867\, \frac{RT_C}{P_C}$$

Soave[9] recently proposed a modification that has been used for calculating equilibrium "k" data very successfully. This change is as follows:

Equation 2-9

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$$

Or

Equation 2-10

$$Z^3 - Z^2 + Z\left(A - B - B^2\right) - AB = 0$$

Where

$$A = \frac{aP}{R^2 T^2}$$

$$B = \frac{bP}{RT}$$

Mixing rules using the interaction coefficients have developed for the constants "a" and "b" or A and B, i.e.

Equation 2-11

$$a_{ij} = (1 - k_{ij})(a_i a_j)$$

where a_{ij} = constant for the a for a mixture of a_i and a_j

k_{ij} = the interaction coefficient for the binary i and j.

Another recent equation that has been proposed is the Peng and Robinson[17] equation, which can be expressed as

Equation 2-12

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)}$$

This equation seems to cover the ranges of temperature and pressure very well. Also most physical properties are calculated close to experimental values.

BWRS and EK equations can be used with liquids or for calculating enthalpies , etc. For example, to use the BWRS for enthalpy, the following equation is used for correcting the effect of pressure on enthalpy:

Equation 2-13

$$H_{T,P} - H_{T,0} = \left(B_0 RT - 2A_0 - \frac{4C_0}{T^2} + \frac{5D_0}{T^3} - \frac{6E_0}{T^4} \right)\rho + 0.5\left(2bRT - 3a - \frac{4d}{T} \right)\rho^2 + 0.2\alpha\left(6a + \frac{7d}{T} \right)\rho^5$$
$$+ \frac{c\rho^2}{T}\left[3\left(\frac{1 - \exp(-\chi\rho^2)}{\chi\rho^2} \right) - 0.5\exp(-\chi\rho^2) + \gamma\rho^2 \exp(-\chi\rho^2) \right]$$

2.2.2 Compressibility Factors

The second type of method is the correction factor method. That is, we apply a correction factor to the ideal gas equation:

Equation 2-14

$$PV = ZRT$$

V = volume of a mole of gas

Z = correction factor and is a function of

Equation 2-15

$$T_r = \frac{T}{T_c}$$

and

$$P_r = \frac{P}{P_c}$$

Figure 16-3 through Figure 16-11 of the GPSA Data book give data on "Z" as a general correlation. To handle mixtures, the law of corresponding states is applied. This is as follows:

"Substances should have similar properties at similar corresponding states. A corresponding state is that distance from the critical temperature or critical pressure expressed on an absolute basis."

This was developed by van der Waal. Thus to handle mixtures we calculate the reduced temperature and pressure for the mixture and then read of f the proper "Z". The "T_c" and "P_c" for mixtures are the so called pseudo values and are the values found by multiplyingthe mole fraction of a component present by the value of the property as if it was a pure compound and then summing the values.

Example Problem 2.1

Find the compressibility factor and the actual density of gas of the composition given in the table below when the gas is at 1000 psig and 100°F.

Comp.	**Mole %**	**T_c°R**	**pT_c**	**Pc psia**	**pP_c**	**Mole wt**	**p Mole wt**	**Comments**
N_2	1.65	227	3.7	492	8.1	28	0.5	
C_1	89.60	343	318.0	668	605.0	16	14.3	
C_2	4.99	550	27.4	710	35.5	30	1.5	
C_3	2.03	666	13.6	616	13.5	44	0.9	
iC_4	0.37	735	2.7	529	2.0	58	0.2	
nC_4	0.62	765	4.7	551	3.4	58	0.4	
iC_5	0.19	830	1.6	483	0.9	72	0.1	
nC_5	0.14	846	1.2	489	0.7	72	0.1	
C_6	0.31	914	2.8	440	1.4	86	0.3	
C_7+	0.10	1024	1.0	362	0.4	114	0.1	Use properties of C_8
			376.7		670.9		18.4	

Therefore:

pseudo T_c = 376.7°R

pseudo P_c = 670.9 psia

average molecular weight = 18.4

Equation 2-16

$$T_r = \frac{T}{T_c} = \frac{560}{376.7} = 1.48$$

Equation 2-17

$$P_r = \frac{P}{P_c} = \frac{1014.7}{670.9} = 1.52$$

From the graph on Figure 16-3 on the GPSA Manual

Z = 0.855

Now find the density of 1 cubic foot at the operating condition

Equation 2-18

$$\rho = \frac{PM_W}{ZRT} = \frac{1014.7(18.4)}{0.855(10.73)(560)} = 3.7\ {}^{lbs}\!/_{cu.ft}$$

This method is pretty good for mixtures of light hydrocarbons or other similar groups of compounds.

Example Problem 1a shows this problem done in Metric units.

1a. The metric values in the problem are

Pressure = 6996 kPa or 69, Atmos.

Temperature = 32°C

or 305°K

T_r and P_r will be the same. The actual density in gram/cc will be

$$\rho = \frac{PM_W}{ZRT} = \frac{69(18.4)}{0.855(82.057)(305)} = 0.059\ {}^{gram}\!/_{cc}$$

Figure 4-13 in Katz[7] shows how well individual compounds compare.

For example at a P_r = 2.0 the "Z" for C_l , C_3 and C_5 is shown in Table 2.4.

Table 2.4: Comparison of Compressibility Factors

"Z" Values				
T_r	C_l	C_3	C_5	From NGPSA Manual For Gas at These Conditions
1.1	0.39	0.405	0.415	.37
1.2	0.575	0.595	0.620	.55
1.3	0.700	0.740	0.755	.685
1.5	0.840	0.880	0.905	.820

However the generalized compressibility chart can be used with good accuracy for light hydrocarbons with less than 5% N_2 present. It was developed by Standing and Katz[10]

For natural gases in which composition is not known, on Fig. 16-6 of the GPSA Data Book gives the pseudo critical pressure and temperatures versus gas gravity. It should be noted that the pseudo critical temperature and pressure are not necessarily anywhere near actual values. Consider a phase envelope as shown in Figure 2.1.

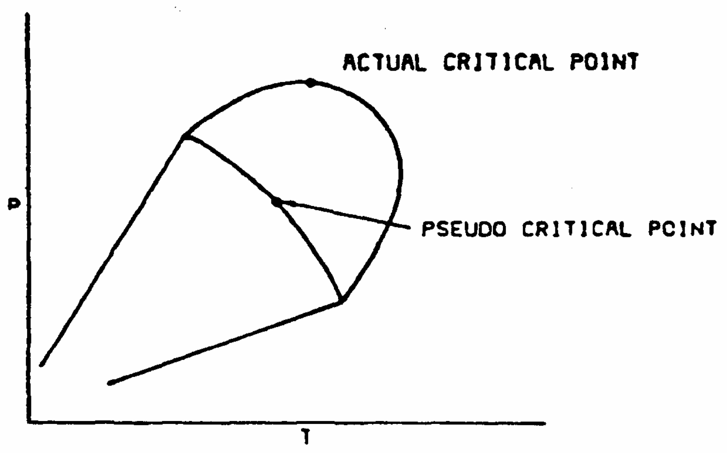


Figure 2.1: Actual and Pseudo Critical Points

For gas mixtures containing significant quantities of sour gas the “z” is not correct as calculated from the Standing Katz chart. A method has been developed by E. Wichert and K. Aziz at the University of Calgary. This method is quite simple and has been Checked by Comparison of over 1000 actual measurements. The authors have also developed a more detailed method using the Redlich Kwong equation that is applicable to a computer. The actual computer program is available through the CNGPA Research program.[12]

The simple graphical method depends on finding "ε" the pseudo critical temperature adjustment factor. This factor is a function of the % of H_2S and CO_2 present. Figures 2.2 and 2.3 show this. Figure 2.3 is just a blow up of the data at lower % acid gas. The method is as follows:

1. Calculate the pseudo T_c and pseudo P_c for a mixture in the regular manner.
2. Find value for "ε" depending on the composition.
3. Find sour gas pT_c' from

Equation 2-19

$$pT_c' = pT_c - \varepsilon$$

4. Find sour gas pP_c' from
   B is the mole fraction of H_2S in the gas.

Equation 2-20

$$pP_c' = \frac{pP_c \, pT_c'}{pT_c + B(1-B)\varepsilon}$$

where B is the mole fraction of H_2S in the gas

5. Calculate pseudo reduced temperature and pressure using above data.
6. Read "Z" from regular Standing and Katz chart, Fig. 16-3 GPSA Data book.

Example problem #2 shows how this is done.

Find the compressibility factor for the gas of the composition given below and compare it with the measured value of 0.671 at 2000 psig (13,890 kpa) and 80°F (26.6°C . The pseudo critical pressure for the mixture is 834 psia (5750 kpa) and the pseudo critical temperature 432°R (240°K).

Composition	
	Mole %
N_2	0.66
H_2S	25.65
CO_2	4.73
C_I	67.57
C_2	0.56
C_3+	0.83
	100.00

Using the regular method of finding the reduced pressures and temperatures we get:

Equation 2-21

$$P_r = \frac{2014}{834} = 2.44$$

Equation 2-22

$$T_r = \frac{540}{432} = 1.25$$

From the graph on Figure 16-3 of the GPSA Manual,

Z = 0.585

Next check by Wichert and Aziz method.

English Units **Metric Units**

Equation 2-23

$$pT_c{}' = 432 - 31 = 401$$

$$240 - 17 = 223$$

Equation 2-24

$$pP_c{}' = 834\left(\frac{401}{432+6}\right) = 770$$

$$5750\left(\frac{223}{240+3.28}\right) = 5270$$

Equation 2-25

$$SourGas\ T_r = \frac{540}{401} = 1.36$$

$$\frac{300}{223} = 1.35$$

Equation 2-26

$$SourGas\ P_r = \frac{2014}{770} = 2.62$$

$$\frac{13890}{5212} = 2.64$$

Equation 2-27

$$SourGas\ Z = 0.69$$

$$0.69$$

Measured value was about 0.671.

Note: Whenever you have a sour gas containing 10% or greater acid gases you should probably correct the compressibility factors by using one of the sour gas correction factor methods.

If further refinement of "Z" is necessary (i.e. with liquids present, H_20, N_2 or various unusual compounds such as could be more expected in petrochemical work) , then we can modify "Z" by use of the "acentric" factor "ω" and the value of "Z" for a simple fluid and the deviation from a simple fluid:

Equation 2-28

$$Z = Z^0 + \omega Z'$$

Z° is the compressibility factor for a simple fluid

Z′ is the compressibility factor correction for deviation from a simple fluid.

ω acentric factor is a measure of deviation from an idealized simple fluid (argon, krypton, etc.)

$$\omega = -\left(\log P_r^{\ 0} + 1.00\right) \qquad at\ T_r = 0.700$$

or by the equation

Equation 2-29

$$\omega = \frac{3}{7}\,\frac{\log {P_c}/{14.7}}{\dfrac{T_c}{T_B} - 1.00} - 1.00$$

where

P_c = critical pressure

T_c = critical temperature

T_B = Boiling point

This equation can be used for mixtures when individual "ω" are not available. Figure 16—21 GPSA Data Book gives some data for "ω".

To find Z° and Z' figures 2.4 and 2.5 can be used. These are charts reproduced from an article by K.S. Pitzer[5].

To actually find Z for a gas the following procedure is used:

1. Find "ω" for a gas mixture by multiplying the value x for each compound by the mole fraction of each component present.
2. Find Z° and Z' from figures 2.4 and 2.5 after finding the systems P_r and T_R

To see the effect of this change the following comparison between NH_3 and CH_4 is given in Table 2.5.

Table 2.5: Actual Compressibilities CH_4 and NH_3

Reduced Pressure (P_r)	2.0		2.0	
Reduced Temperature (T_r)	1.0		2.0	
Z°	0.330		0.958	
Z'	- 0.123		+ 0.155	
	CH_4	NH_3	CH_4	NH_3
ω	0.013	0.250	0.013	0.250
$\omega Z'$	- 0.0016	- 0.0308	+ 0.0020	+ 0.0383
$Z = Z^\circ + \omega Z'$	0.328	0.299	0.960	0.997

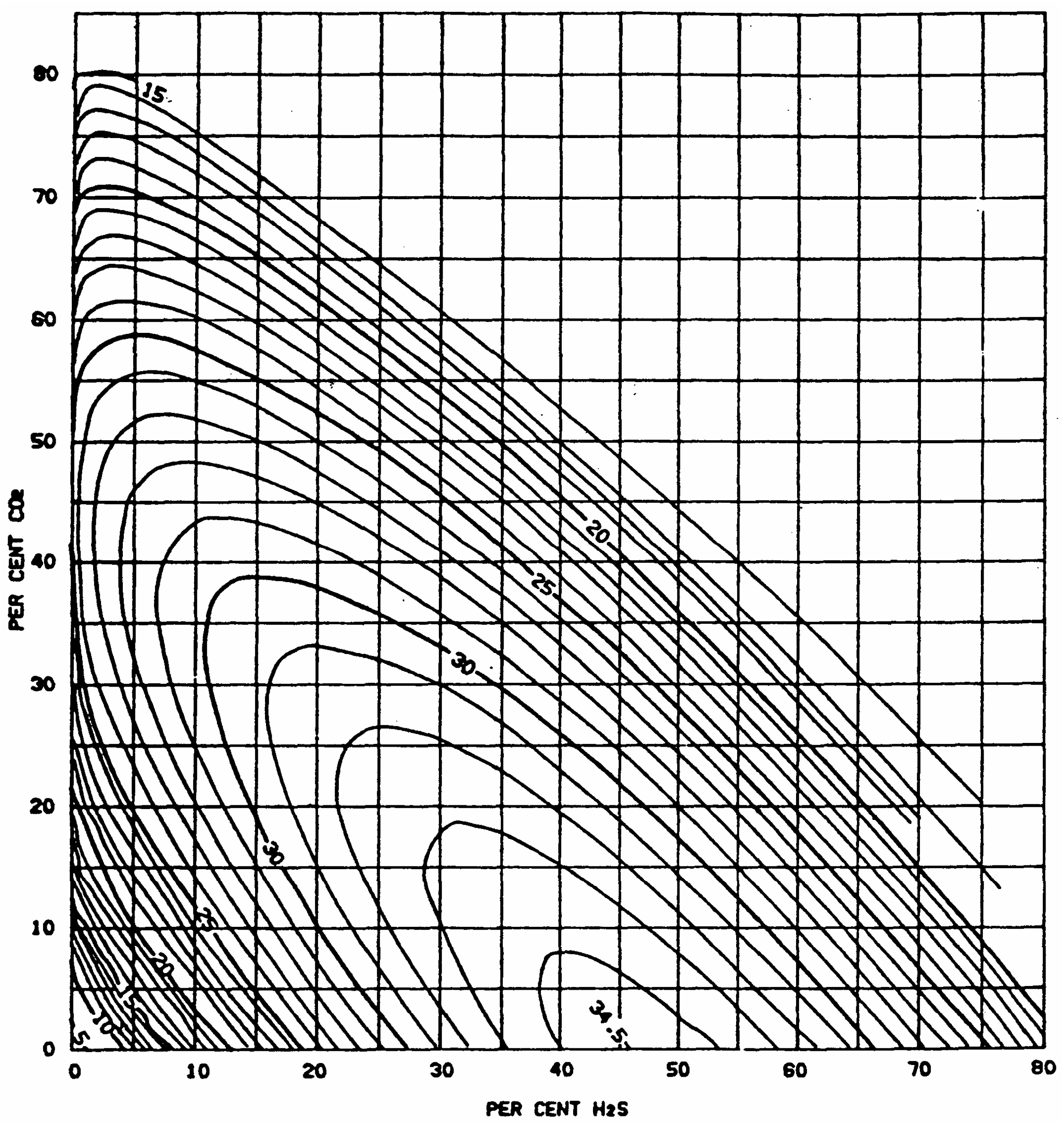


Figure 2.2: Pseudo Critical Temperature Correction Factor, ε, °F

See Metric GPSA Data Book for values in °C

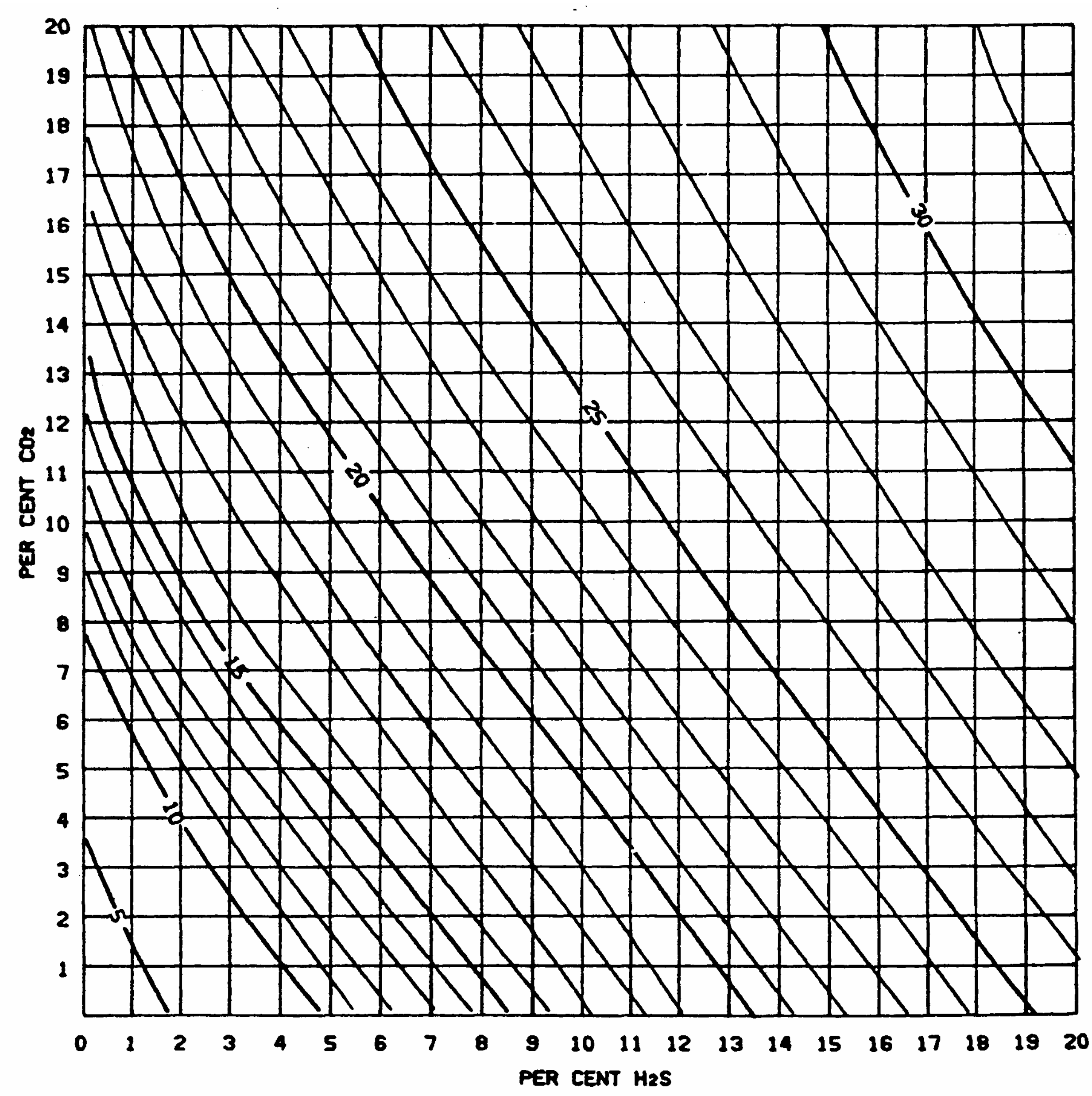


Figure 2.3: Pseudo Critical Temperature Correction Factor, "Normal Operating Range", ε, °F

See Metric GPSA Data Book for values in °C

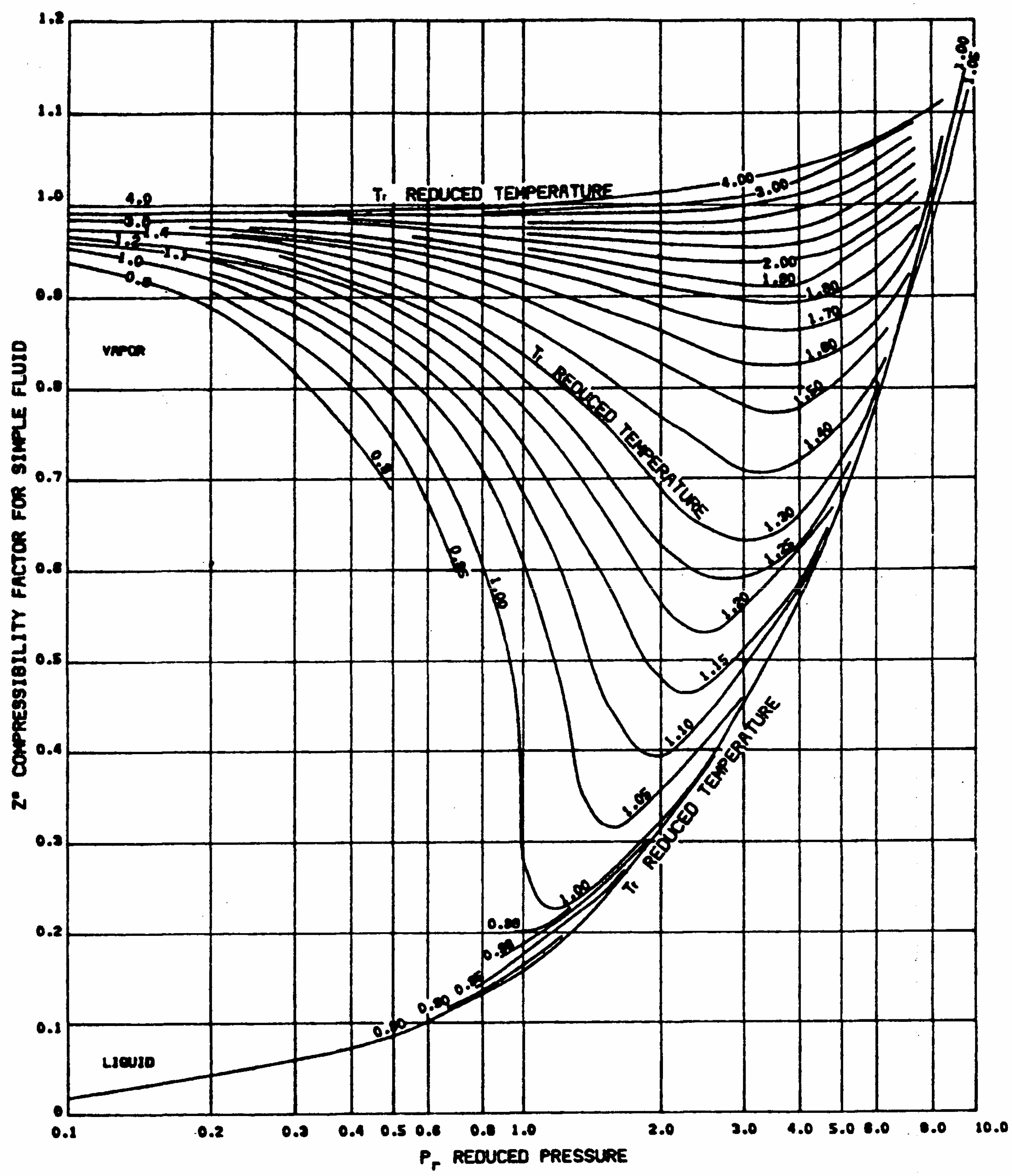


Figure 2.4: Generalized Compressibility Factor for Simple Fluid

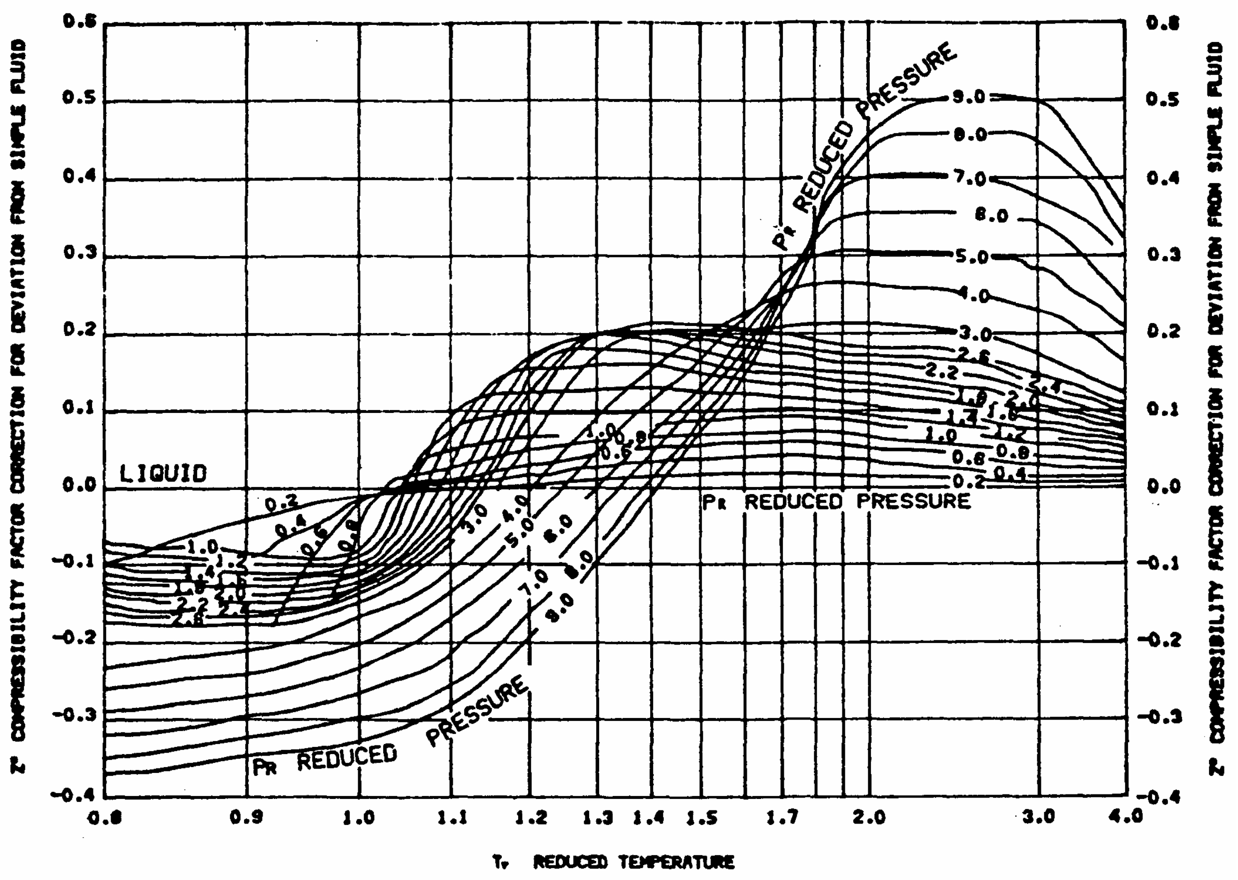


Figure 2.5: Generalized Compressibility Factor Correction for Deviation from Simple Fluid

2.2.3 Liquid Densities

For liquids at low pressures and room temperatures the liquid volumes are additive and the liquid density can be calculated from the composition and temperature density charts (Fig. 16-IZ, GPSA Data Book). This procedure assumes ideal solutions. Note that methane and ethane data are given as the apparent density. Another way is to calculate density exclusive of C_1 and C_2 and use the chart on P. 167 of the GPSA Manual (1966 Ed.) to find system with C_1 and C_2. This procedure is based on the equation

Equation 2-30

$$V = x_{c1}\overline{V}_{c1} + x_{c2}\overline{V}_{c2} + \sum_{i=3}^{n} x_{ci}\overline{V}_{c1}$$

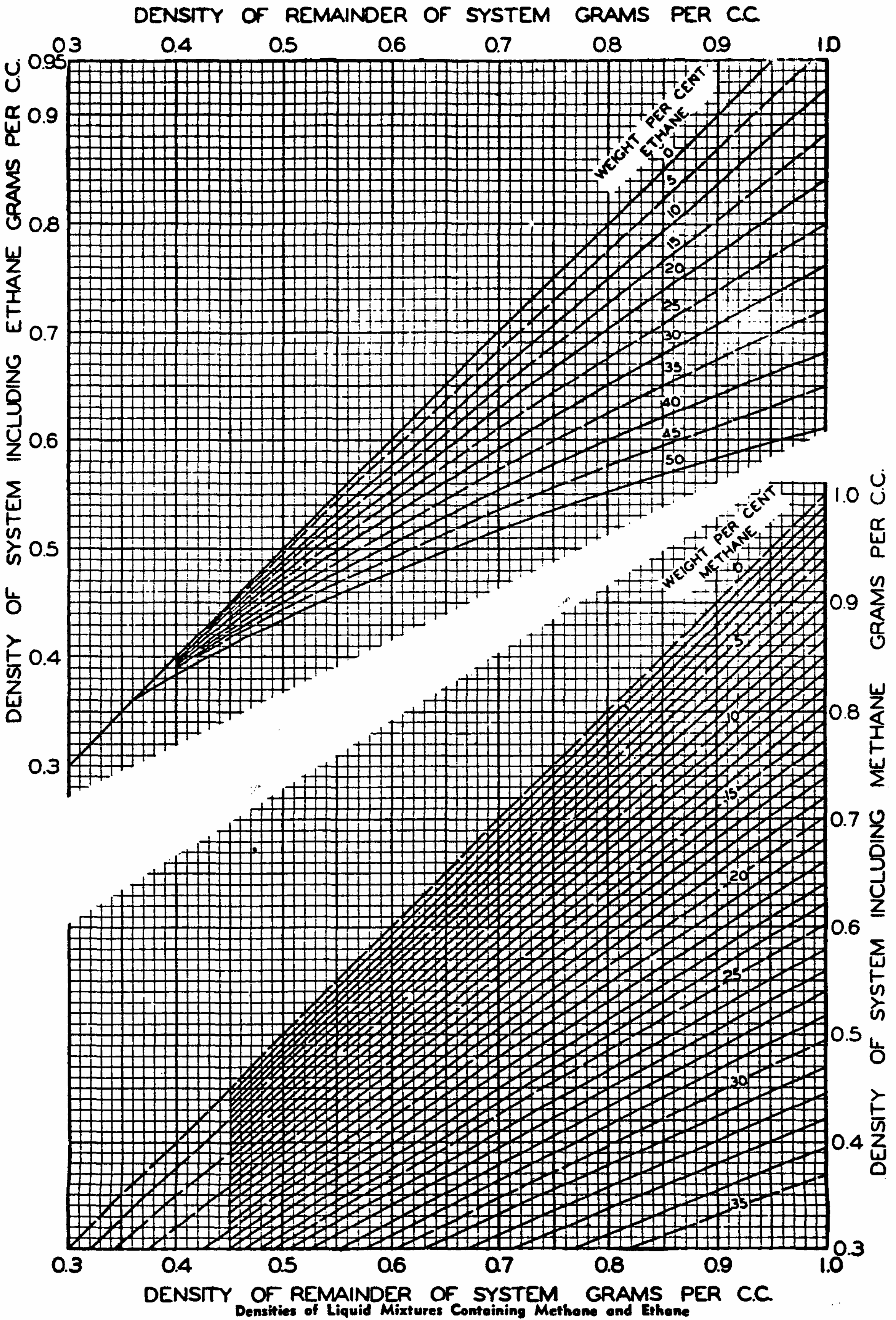
where $\overline{V}_{c1}$ and $\overline{V}_{c2}$ are the effective molar volumes of methane and methane. Figure 2.6 gives the data for this calculation.

At high pressure it is necessary to correct the density. Figure 16-15 GPSA Data Book shows how to do this.

The various equations of state, i.e. the BWRS, the Redlich Kwong, Soave and the Peng-Robinson methods, can also be used to calculate liquid densities as well. In fact most cou~uter programs of these equations give both the liquid and gas densities of a two-phase mixture.

2.2.4 Density of Cryogenic Liquids

As the temperatures of separation decrease any liquids produced contain increasing amounts of methane and ethane. Equation 31 (and Table 2.6 and Table 2.7) expresses an empirical density correlation for liquified natural gas (LNG). It is for liquids with a molecular weight less than 33, containing less than 5 mole % nitrogen, oxygen and isoparaffins, in the temperature range -140 to -184°C (-220 to -300°F)



Densities of Liquid Mixtures Containing Methane and Ethane

From "Natural Gasoline and the Volatile Hydrocarbons", by Brown, Katz, Oberfell, and Alden. Natural Gas Processors Association, 1948.

Figure 2.6: Density of Remainder of System Grams Per CC

Equation 2-31

$$\rho = \frac{\sum x_i M_i}{\sum (x_i V_i) - x_m C}$$

where:

ρ = density in kg/cu meter

x_i = mol. fr. of component "i"

M_i = mol. wt. of component "i"

V_i = molar volume of "i" from Table 2.6

x_m = mol. fr. of methane

C = correction factor for volume reduction from Table 2.7

2.3 Thermodynamic Properties

The next set of physical properties to discuss are thermodynamic properties. These include enthalpy, or heat capacity, latent heats and specific heats.

2.3.1 Outline of Properties

Enthalpy or Heat Capacity

"H" is the total amount of heat required to raise a unit of mass to a predetermined temperature and pressure from a base temperature and pressure.

Equation 2-32

$\Delta H = \Delta E + \Delta PV$ *for a substance*

where:

E is the internal energy

P is the pressure

V is the specific volume

Table 2.6: Molar Volumes of Individual Components

Component	Mol. Mass kg/kmole	-175°C	-170°C	-165°C	-160°C	-155°C	-150°C	-145°C	-140°C
CH_4	16.042	0.03636	0.03696	0.93757	0.03821	0.03890	0.03964	0.04042	0.04126
C_2H_6	30.068	0.04682	0.04721	0.04760	0.04800	0.04841	0.04882	0.04925	0.04969
C_3H_8	44.094	0.06122	0.06164	0.06208	0.06252	0.06298 .	0.06344	0.06392	0.O644O
n-C_4H_{10}	58.120	0.07543	0.07589	0.07635	0.07682	0.07729	0.07778	0.07826	0.07876

i-C_4H_{10}	58.120	0.07557	0.07608	0.07659	0.07711	0.07764	0.07818	0.07873	0.07928
n-C_5H_{12}	72. 146	0.08894	0.08944	0.03995	0.09047	0.09099	0.09152	0.09206	0.09260
i-C_5H_{12}	72.146	0.00957	0.09008	0.09060	0.09113	0.09167	0.09221	0.09275	0.09330
n-C_6H_{14}	86.172	0.10326	0.10380	0.10434	0.10489	0.10545	0.10602	0.10659	0.10716
N_2	28.016	0.03996	0.04181	0.04407	0.04683	0.05021	0.05428	0.05915	0.08496
O_2	32.00		0.02980	0.03061	0.03151	0.03252	0.03367		

Molar Volume, m^3/kmole, at various temperatures

Table 2.7: Correction, C, for Volume Reduction of LNG Mixtures

Molecular Mass of Mixture x_1 M_1	**-140°C**	**-145°C**	**-150°C**	**-155°C**	**-160°C**	**-165°C**	**-170°C**	**-175°C**
16.0	0	0	0	0	0	0	0	0
16.2	0.06	0.05	0.05	0.04	0.04	0.04	0.03	0.03
16.4	0.13	0.12	0.122	0.10	0.10	0 -09	0.08	0.07
16.6	0.20	0.18	0.17	0.16	0.15	0.13	0.12	0.11
16.8	0.26	0.25	0.23	0.21	0.19	0.19	0.16	0.15
17.0	0.33	0.31	0.29	0.27	0.24	0.23	0.21	0.19
17.2	0.40	0.37	0.35	0.32	0.30	0.27	0.25	0.23
17.4	0.47	0.44	0.40	0.38	0.35	0.32	0.30	0.27
17.6	0.54	0.49	0.46	0.43	0.40	0.37	0.34	0.31
17.8	0.60	0.55	0.51	0.48	0.44	0.41	0.38	0.35
18.0	0.66	0.61	0.57	0.53	0.49	0.45	0.42	0.38
18.5	0.81	0.75	0.70	0.65	0.60	0.56	0.52	0.48
19.0	0.95	0.88	0.82	0.76	0.71	0.66	0.61	0.57
19.5	1.09	1.01	0.94	0.88	0.81	0.76	0.70	0.65
20.0	1.21	1.13	1.05	0.98	0.91	0.85	0.79	0.74
21.0	1.42	1.34	1.25	1.17	1.10	1.03	0.96	0.89
22.0	1.61	1.53	1.43	1.35	1.26	1.18	1.10	1.03
23.0	1.75	1.65	1.56	1.48	1.39	1.31	1.23	1.15
24.0	1.85	1.76	1.67	1.58	1.49	1.41	1.33	1.26
25.0	1.92	1.83	1.74	1.66	1.58	1.50	1.42	1.34

c x 10 m^3/kmole, at various temperatures

Latent Heat

Heat required for a change of phase can be expressed by Clausius Chapeyron equation:

Equation 2-33

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

Specific Heats

This is defined as the amount of heat required to raise a unit of mass a degree of temperature. They are measured at

Constant pressure Cp

Constant volume Cv

For a perfect gas it can be shown

Equation 2-34

$$Cp = Cv + R \text{ for a mole of a compound}$$

where:

R is the gas constant.

This equation is used in calculating the ratio of specific heats for a mixture which is used in compression calculations.

Entropy - "S"

Another well known property that is used in some calculations is the entropy which depends only on the condition of the system. It can be defined by the equation:

Equation 2-35

$$dS = \frac{dQ}{T}$$

where:

Q is the heat absorbed by the system.

For a change of phase and for most applications we know dQ = dH. Therefore, at a constant temperature and pressure we can write:

Equation 2-36

$$\Delta S = \frac{\Delta H}{T}$$

Free Energy

We also will consider later another thermodynamic property called the free energy F. It is defined by the equation:

Equation 2-37

$$F = H - TS$$

where:

F is a measure of the useful work done exclusive of expansion work.

For a chemical reaction the change of free energy can be expressed by the equation:

Equation 2-38

$$\Delta F^{0} = RT \ln K$$

where:

K is the chemical equilibrium constant.

Also we can write the equation:

Equation 2-39

$$\Delta F^{0}{}_{P-R} = \Delta H^{0}{}_{P-R} - T\Delta S^{0}{}_{P-R}$$

where:

the subscripts P and R respectively represent products and reactants of a chemical equation.

2.3.2 Enthalpies

The enthalpies of pure compounds are given in many tables, in Chemical Engineer's Handbook, in Maxwell[6], in Katz[7] and in the GPSA Data Book. In the Metric GPSA Data Book from Figures 17-4 to 17-9 there are Mollier charts for several compounds. In the new English GPSA Data Book figure numbers are different. These plot enthalpy versus entropy at various temperature, pressures, etc. Similarly, the book "Thermo Properties of Hydrocarbons"[16] gives this data. Also Maxwell, p. 98 onward, gives data on individual compounds.

For mixtures of gases at high pressure there is a problem. It can be shown that

Equation 2-40

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

or with the compressibility factor

Equation 2-41

$$\left(\frac{\partial H}{\partial P}\right)_T = -\frac{RT^2}{P}\left(\frac{\partial Z}{\partial T}\right)_P$$

Katz on P. 133 shows a plot of the change of enthalpy vs P_r at various T_r where P_r is the reduced pressure and T_r is the reduced temperature. A similar graph on P. 134 and P. 136 show the effect with slightly different parameters for enthalpies.

We are interested in mixtures which complicate the calculations. There are several methods. Here are two:

Total Enthalpy Charts

In the GPSA Data Book there are a series of charts giving the enthalpies vs temperatures and mole weights at various pressures. Charts are given for liquids and gas at an ideal gas, 150 psia to 3000 psia. Similar figures and data are given in the metric GPSA book from 1400 to 20,800 kPa. These charts are generally good for gaseous mixtures. The basic assumption in that a mixture of hydrocarbons in vapour state has the same enthalpy of a single compound having the same mole weight as mixture. These charts are good for doing a quick calculation of heat duties.

Curl and Pitzer Method

Another way to calculate the difference in enthalpy at high pressures is to follow the method of R.F. Curl and K.S. Pitzer[20]. This method is explained in detail in the GPSA Data Book, P. 17-1. It makes use of the acentric factor "w" and the use of factors for a simple fluid and the deviation from a simple fluid. The equation used is:

Equation 2-42

$$H^0 - H = RT_C\left[\left(\frac{H^0 - H}{RT_C}\right)^0 + \varpi\left(\frac{H^0 - H}{RT_C}\right)\right]^1$$

where:

H° is the ideal gas enthalpy

H is enthalpy at the desired condition

$\left(\frac{H^0 - H}{RT_C}\right)^0$ = effect of pressure on a simple fluid

$\left(\frac{H^0 - H}{RT_C}\right)^1$ = the correction for the deviation from a simple fluid for pressure.

The values for these items are given in the GPSA Data Book as follows:

H° is plotted vs. temp. in Figure 17-1 & 17-12

ω is given in Figure 16-1 (Pg. 16.3)

$\left(\frac{H^0 - H}{RT_C}\right)^0$ for a simple fluid is given graphically on Figure 17-13.

$\left(\frac{H^0 - H}{RT_C}\right)^1$ is given graphically on Figure 17-14.

To handle mixtures the procedure is to find the

average ω by mole fraction

pseudo T_c by mole fraction

pseudo P_c by mole fraction

Then use these values in the equation given previously.

The example problem given below shows the application of the total enthalpy method.

Example Problem 2.2

Calculate the duty required to chill 100 MMSCFD of a gas at 937 psig of the composition listed below from 40° to 0°F using propane as a refrigerant.

Component	Mole %
N_2	0.00
C_1	95.62
C_2	3.01
C_3	0.67
iC_4	0.18
nC_4	0.20
iC_5	0.09
nC_5	0.09
C_6+	0.14

Solution

First find the amount of heat to be removed in the chillers. This is found by enthalpy calculations. Let's first see if there is much liquid condensed. Run a flash calculation at 0°F. Assume P_k = 3000 psia. The following is the result of a computer flash calculation:

Comp.	Moles of Feed	$k^{937}{}_0$	Moles Vapour	Moles Liquid	Mole Wt	P Mole Wt. of Vapour	P Mole Wt. Mix	P Mole Wt. Liquid
C_1	95.62	2.174	95.586	0.044	16	15.29	15.30	9.26
C_2	3.01	0.457	3.005	0.006	30	0.91	0.90	2.36
C_3	0.67	0.131	0.666	0.005	44	0.29	0.29	2.89
iC_4	0.18	0.065	0.177	0.003	58	0.10	0.10	2.29
nC_4	0.20	0.046	0.196	0.005	58	0.10	0.11	3.81

iC_5	0.09	0.018	0.086	0.004	72	0.06	0.06	3.79
nC_5	0.09	0.014	0.086	0.004	72	0.06	0.06	3.79
C_6+	0.14	0.004	0.119	0.004	84	0.11	0.12	4.42
			99.923	0.076		16.92	16.94	32.61

Let us use the enthalpy chart method. We will use primarily the 1000 psia chart.

Number of lbs. flowing:

$$\frac{100,000,000}{379}\frac{16.94}{24} = 186,235 \quad lbs/hr$$

$H_{40°F}$ = 200 BTU's/lb. (Figure 17-12 GPSA Data Book)

$H_{O°F}$ = 170 for gas (Figure 17-14 GPSA Data Book)

$H_{O°F}$ = -10 for liquid (Figure 17-14 GPSA Data Book and mole wt of 32.6)

Heat Content Inlet

= 200 (186,235)

= 37,247,000 BTU/hr.

Heat Content Outlet (convert mole liquid a gas % to mass %)

Vapour = 170 (186,235) (.9985)

Liquid = -10 (186,235) (.0015)

Total = 31,609,466 B'IU's/hr

Duty (Difference) = 5,037,534 BTU's/hr

Now let us do the problem in metric units.

Flow is 283,100 m^3/day

Pressure is 6556 kPa

Temperature is 4.4C in and -17.7 out.

Kg flowing = $\frac{2.831,000}{23.6}\frac{16.94}{24} = 84670 \; kg/hr$

= 84670 kg/hr

at 6200 kPa - Figure 17-11 SI GPSA Data Book

$H_{4.4}$ = 500 KJ/kg gas

$H_{-17.7}$ = 440 KJ/kg gas

$H_{-17.7}$ = -105 KJ/kg liquid (MW = 32.6)

Heat Content Inlet

84670 (500) = 42,335,000 KJ/hr

Heat Content Out:

Vapour = 440 (84670)(.9985)

= 37,198,918 kJ/hr

Liquid = -105(84670)(.0015) = -13,335kJ/hr

Total = 37, 185,583 kJ/hr

Duty (Difference) = 5,149,417 kJ/hr

= 1440.4 KW

2.3.3 Correlation Methods

All the various correlations i.e. BWRS, Soave, Redlich Kwong, Prausnik, etc. give enthalpy data for each individual mixture. These of course are more accurate and should be used for detailed design.

A study of J. Powers (presented at the 1971 Annual Convention of the NGPA) showed the results of 8 different enthalpy correlations at temperatures from -250°F to +250°F

-156°C to +121°C) and at pressures from 0 psig to 2000 psig (101 to 13890 kPa). Here are the average deviations of the values of some of the important correlations.

% Deviation from Actual Value

	% Deviation from Actual Value
Power's Generalized Correlation	1.57
Rice Property III	1.60
Modified BWR	1.67
CPY	3.46
Johnson & Colver	2.04
NGPA - old values	11.88
NGPA - new values	2.00

The newer Soave, Peng Robinson correlations give much better accuracy.

We have been discussing essentially the enthalpies of gas. We should also discuss liquids and mixtures of liquids. For systems that remain liquid the difference in enthalpy between two temperatures is found by multiplying $C_p(T_1 - T_2)$ or subtracting the enthalpies. Figures 17-14 and 17-15 of the GPSA Data Book gives enthalpies of saturated liquids. When we have liquids and vapours occurring together we have to take into account the heat accompanying a change of phase or the latent evaporization or condensation. Latent heats for pure compounds can be found from the thermo property tables or the Mollier diagrams given in the GPSA Data Book from the data in Maxwell, p. 94 to 127.

To handle the case of compounds at conditions above their critical points but still in a liquid, use the data shown in Maxwell for gases in solution, shown in Figure 2.7.

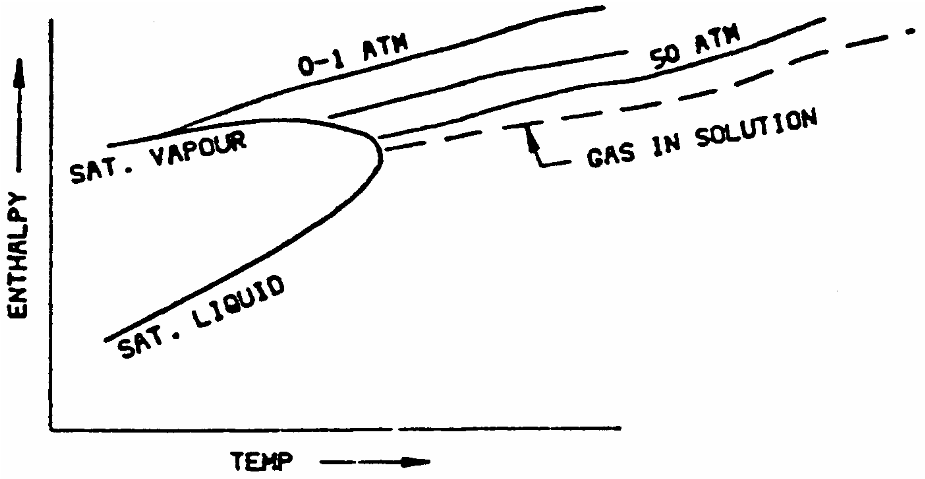


Figure 2.7: Enthalpy of Gases in Solution

Therefore- the procedure when we have either vapourization or condensation occurring in an exchanger is to calculate composition of vapour and liquid at outlet condition as well as at the inlet conditions. Then proceed as follows:

> If you are chilling a rich gas in which there is lots of condensation and you wish to find heat duty:

1. Find enthalpy at inlet temperature and pressure
2. Run a flash calculation at outlet temperature and pressure to see amount and composition of liquid and gas phases. Calculate the weight fraction of liquid and gas present.
3. Calculate enthalpy of each phase at outlet conditions using compositions found from 2.
4. Multiply each enthalpy by the wei~it fraction of the appropriate phase and add enthalpies together.
5. Subtract enthalpy in 1) from 4) and multiply by lbs/hr flow rate to find duty in BTU' s per hour.

2.3.4 Processes Using Enthalpy

Joule Thomson Expansion. This is expressed by the equation

Equation 2-43

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H$$

where:

μ = Joule-Thomson coefficient

This type of expansion occurs through a throttling valve, i.e. a well choke or a refrigeration chiller feed valve. The process occurs at constant enthalpy. Therefore, the Mollier type diagram can be used to find the temperature on a change of pressure. Also a chart such as Figure 15-23 of the GPSA Data Book on page 15-17, can be used. Further, National Tank has published a good chart on thAs, as shown in H_2S are present in the gas. This has been discovered by some field work by G. Palmer and others of Maloney Steelcraft Ltd.

2.3.5 Process Using Entropy

Adiabatic compression or expansion takes place at constant entropy. Thus the Mollier chart can also be used in this regard. See pg. 17-19 of GPSA Data Book for further explanation of this calculation. This is particularly important in compressor and expander calculations.

2.4 Heats of Combustion

The next property to mention is the heating value or the heat of combustion. These are two kinds of heating values:

6. *Gross Value* - This is the value obtained by measuring the heat formed and cooling the products of combustion to 600F including condensing the water vapour. A very important part of the calculation of this value is the reference state, i.e. BTU's/lb weight in a vacuum or air, whether it is ideal gas or liquid or whatever. The GPSA has set up a standard for this calculation for mixture. The ideal gas heating value is calculated by the equation:

Equation 2-44

$$H_{ideal} = \sum_i x_i H_i$$

where x1, x2 .... x,, are the mole fraction of each component. H1, H2 .... H,, are the ideal gas heating values from Table 2.6 for each component. The real gas heating value H is set by the equation:

Equation 2-45

$$H_r = \frac{H_{ideal}}{Z}$$

Z is found from

Equation 2-46

$$Z = 1 - \left(x_1 \sqrt{b_1} + x_2 \sqrt{b_2} + \ldots\ldots.. + x_n \sqrt{b_n} \right)^2$$

A correlation for H if present is also given in the GPSA Data Book. Data for equation 2-45 is also found in Table 2.8 or Metric values in 2.9. GPSA Standard 2172-72 explains this calculation further as does page 16-34 of the GPSA Data Book. Gas specific gravity can also be calculated using equation 2-45.

Net Value - In this case the water is not considered to be condensed. In most applications in the gas industry the gross heating value is used. In older gas contracts the gross value is stated as saturated with water vapour at 60°F and 30" Hg pressure. To find the heating value in this case multiply the gross dry basis by 0.9825. A calorimeter on pipelines measures the heat content as saturated with water vapour. The newer contracts just take a continuous sample, analize same and then calculate the gross heating value using the latest GPA data.

Table 2.8: Properties of Natural Gas Components (Imperial)

Component	Ideal Gas Specific Gravity	Ideal Gas Heating Value [a] Btu/cf at 60°F, 1atm (760 mm Hg)	Comppressibility Factor [b] Z, at 60°F, 1 atm	Summation Factor, $\sqrt{b}$
Hydrocarbons				
Methane	0.5539	1009.7	0.9981	0.0436
Ethane	1.0382	1768.8	0.9916	0.0917
Propane	1.5225	2517.5	0.9820	0.1342
Isobutane	2.0068	3252.7	0.9696	0.1744
n~Butane	2.0068	3262.1	0.9667	0.1825
Isopentane	2.4911	4000.3	0.9482 (f)	0.2276
n-Pentane	2.4911	4009.6	0.9435 (f)	0.2377
n-Hexane	2.9753	4756.2	0.920 (f)	0.283
n-Heptane(g)	3.4596	5502.8	0.920 (f)	0.283
Hexanes plus	(h)	(h)	(h)	
Nonhydrocarbons				
Air	1.0000	----	0.99959	0.0202
Carbon Dioxide	1.5195	----	0.99432	0.0640 (d)
Carbon Monoxide	0.9671	321.37	0.99953	0.0217
Helium	0.1382	----	1.00048	-0.017 (e)
Hydrogen	0.0696	325.02	1.00060	----
Hydrogen Sulfide	1.1765	637 (c)	0.9903	0.0985
Nitrogen	0.9672	----	0.99973	0.0164
Oxygen	1.1048	----	0.99927 (i)	0.0270

a) NGPA Publication 2145-71: "Physical Constants of Paraffin Hydrocarbons and Other Components of Natural Gas" for hydrocarbons; IGT Bulletin 32 for nonhydrocarbons.

b) ASTM DS 4A: "Physical Constants of Hydrocarbons C1 to C,~5" for C, - C4; IGT Bulletin 32 for other components.

c) For combustion to gaseous SO2.

d) Pseudo value for mixtures containing less than 20 % CO2.

e) Pseudo value for mixtures containing less than 1 % He.

f) For the hypothetical gas.

g) Applicable for mixtures containing less than 0.05 percent heptanes.

h) Properties of hexanes plus fractions may vary widely, and should be determined, by a mutually agreeable method.

i) AGA Report No. 3, 1969.

Note: To prevent confusion, note that Ideal Specific Gravities shown in IGT Bulletin No. 32 are based on 1961 molecular weights and referenced to real air; values in this Table are based on 1969 molecular weights and ref evenced to ideal air.

Table 2.9: Properties of Natural Gas Components (Metric)

Component	Ideal Gas Relative Density	Ideal Gross Heating Value [a] Mj/m^3 @ 15°C, 101.325 kPa (abs)	Comppressibility Factor [b] Z @ 15°C, 101.325 kPa (abs)	Summation Factor, $\sqrt{b}$
Hydrocarbons				
Methane	0.5539	37.694	0.9981	0.0436
Ethane	1.0382	66.032	0.9915	0.0922
Propane	1.5225	93.972	0.9810	0.1378
Isobutane	2.0068	121.426	0.9665	0.1830
n~Butane	2.0068	121.779	0.9641	0.1895
Isopentane	2.4911	149.319	0.948 (f)	0.2280
n-Pentane	2.4911	149.654	0.942 (f)	0.2408
n-Hexane	2.9753	177.556	0.910 (f)	0.3000
n-Heptane(g)	3.4596	205.43 1	0.852 (f)	0.3847
Hexanes plus	(h)	(h)	(h)	
Nonhydrocarbons				
Air	1.0000	----	0.9996	0.0200
Carbon Dioxide	1.5195	----	0.9943	0.0640(d)
Carbon Monoxide	0.9671	----	0.9995	0.0224
Helium	0.1382	----	1.0005	-0.017 (e)
Hydrogen	0.0696	12.091	1.0006	----
Hydrogen Sulfide	1.1765	23.791(c)	0.9903	0.0985
Nitrogen	0.9672	----	0.9997	0.0173
Oxygen	1.1048	----	0.9993 (i)	0.0265

a) GPSA Engineering Data Book (SI), Fig. 16-1.

b) For combustion to gaseous 502.

c) Pseudo value for mixtures containing less than 20% 002.

d) Pseudo value for mixtures containing less than 1% He.

e) For the hypothetical gas.

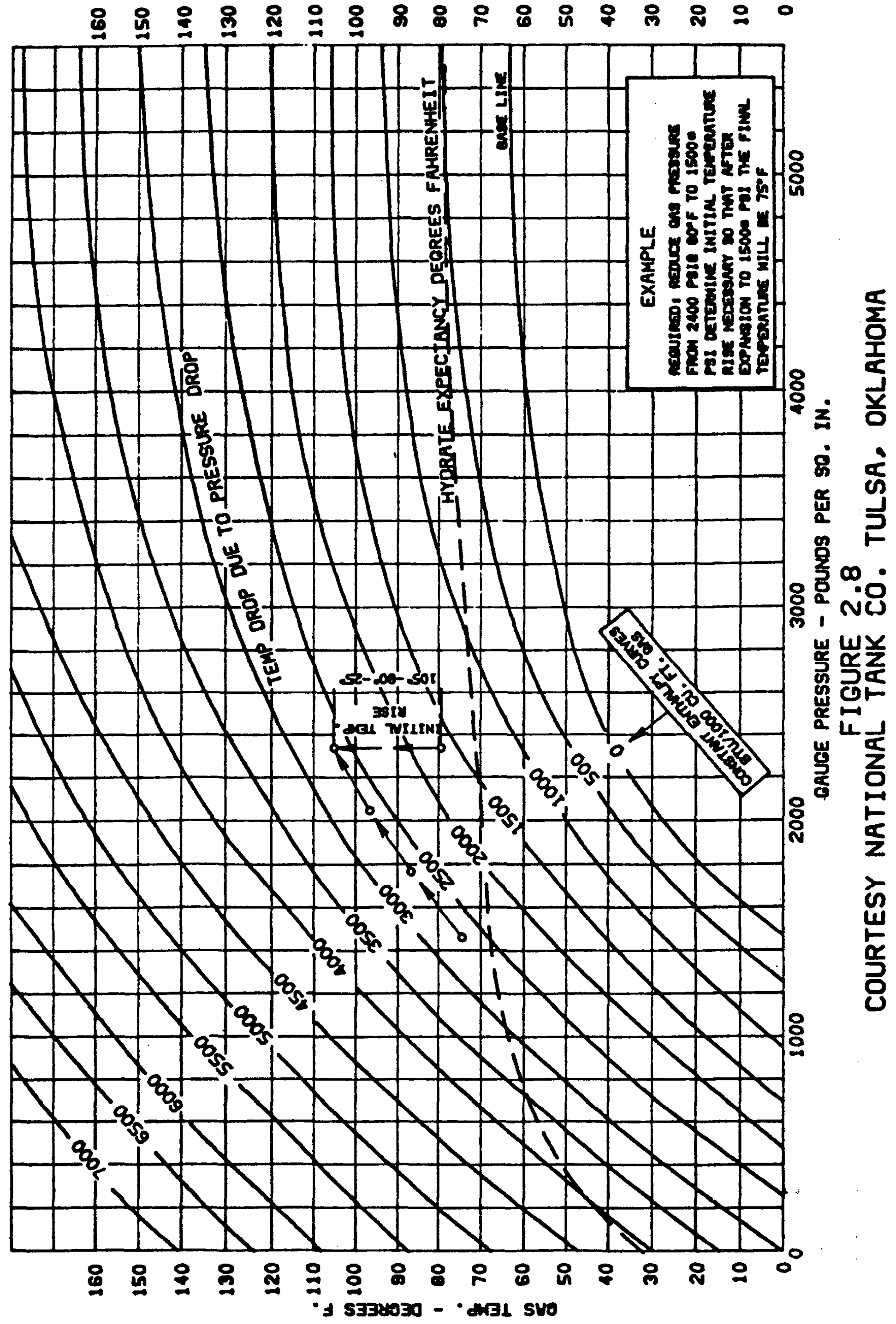
f) The error in calculating heating value is less than 0.05% when the gas contains less than 1% of C6 paraffin.

g) and C, aromatics and less than 0.05% of 01+ paraffins and C9+ aromatics.

h) Properties of hexanes plus fractions may vary widely, and should be determined by a mutually agreeable method.

i) AGA Report No.3,1969.

Note: Ib prevent confusion, note that Ideal Specific Gravities (Relative Densities) shown in LGT Bulletin No. 32 are based on 1961 molecular masses and referenced to real air; values in this Table are based on 1969 molecul,ar masses and referenced to ideal air.



EXAMPLE

REQUIRED: REDUCE GAS PRESSURE FROM 2400 PSIG 80°F TO 1500# PSI DETERMINE INITIAL TEMPERATURE RISE NECESSARY SO THAT AFTER EXPANSION TO 1500# PSI THE FINAL TEMPERATURE WILL BE 75°F

Figure 2.8: Natural Gas Expansion-Temp. Reduction Curve Based on .7 Sp. Gr. Gas

2.5 Viscosity

Another important property is viscosity. It is defined by:

$$\mu = \frac{Shearing\ Stress}{Rate\ of\ Shear\ Stress}$$

It is the internal friction in a fluid that reduces fluid flow. Viscosity is measured normally in metric units of centipoise. Multiply by .000672 to convert to British Units. (lb/ft sec.)

2.5.1 Liquids

Data for liquids is given on Fig. 16-23 of the GPSA Data Book. Here the viscosity in centipoise is plotted versus temperature. A much more extensive discussion is given in the chapter on viscosity in Maxwell[6]. The conversion from absolute viscosity to other types of viscosity are given in the GPSA Data Book, i.e. Kinematic Saybolt, etc. Except at very high values pressure does not affect viscosity. The viscosity of liquid sulphur is quite special; it increases with temperature. Figure 2.9 shows the data.

2.5.2 Gases

Figure 16-27 (Fig. 16-25 in metric version) of the GPSA Data Book gives the viscosity of gases at low pressure (essentially atmos.) 7. for hydrocarbons. Similarly Katz[7] gives data for individual compounds on Pg. 169, 170. Note that N_2, $C0_2$, H_2S air are more viscous at same temperature as compared to hydrocarbons.

The viscosity of gas at high pressure can be found by use of Fig. 16-24 of GPSA Data Book which plots temperature vs. viscosity vs. gravity at different pressures. Another way is to calculate the reduced temperature and reduced pressure and use. Fig. 16-28 in the GPSA Data Book which gives a ratio μ at high pressure vs μ atmospheric pressure.

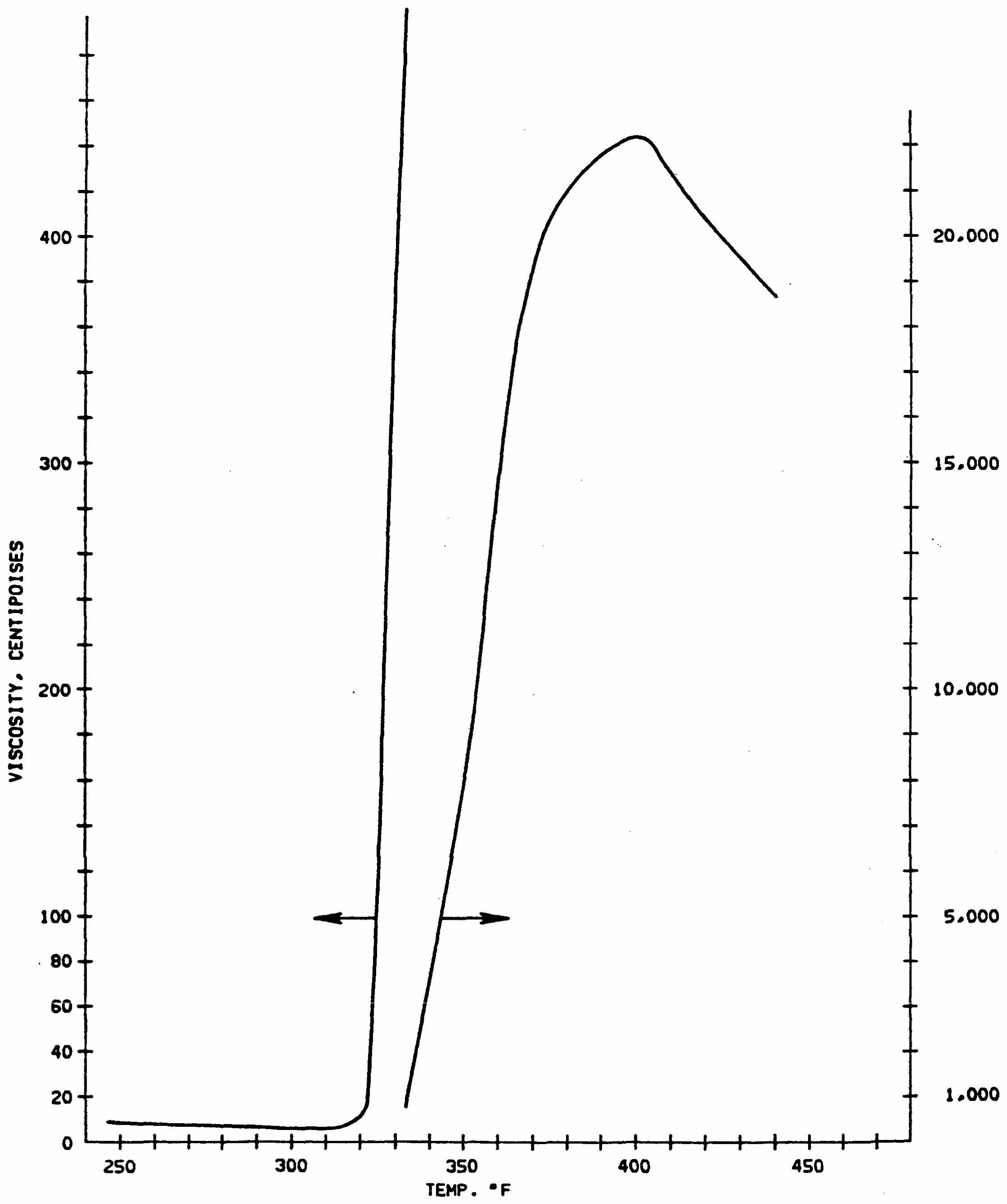


Figure 2.9: Effect of Temp. on Viscosity of Molten Sulphur

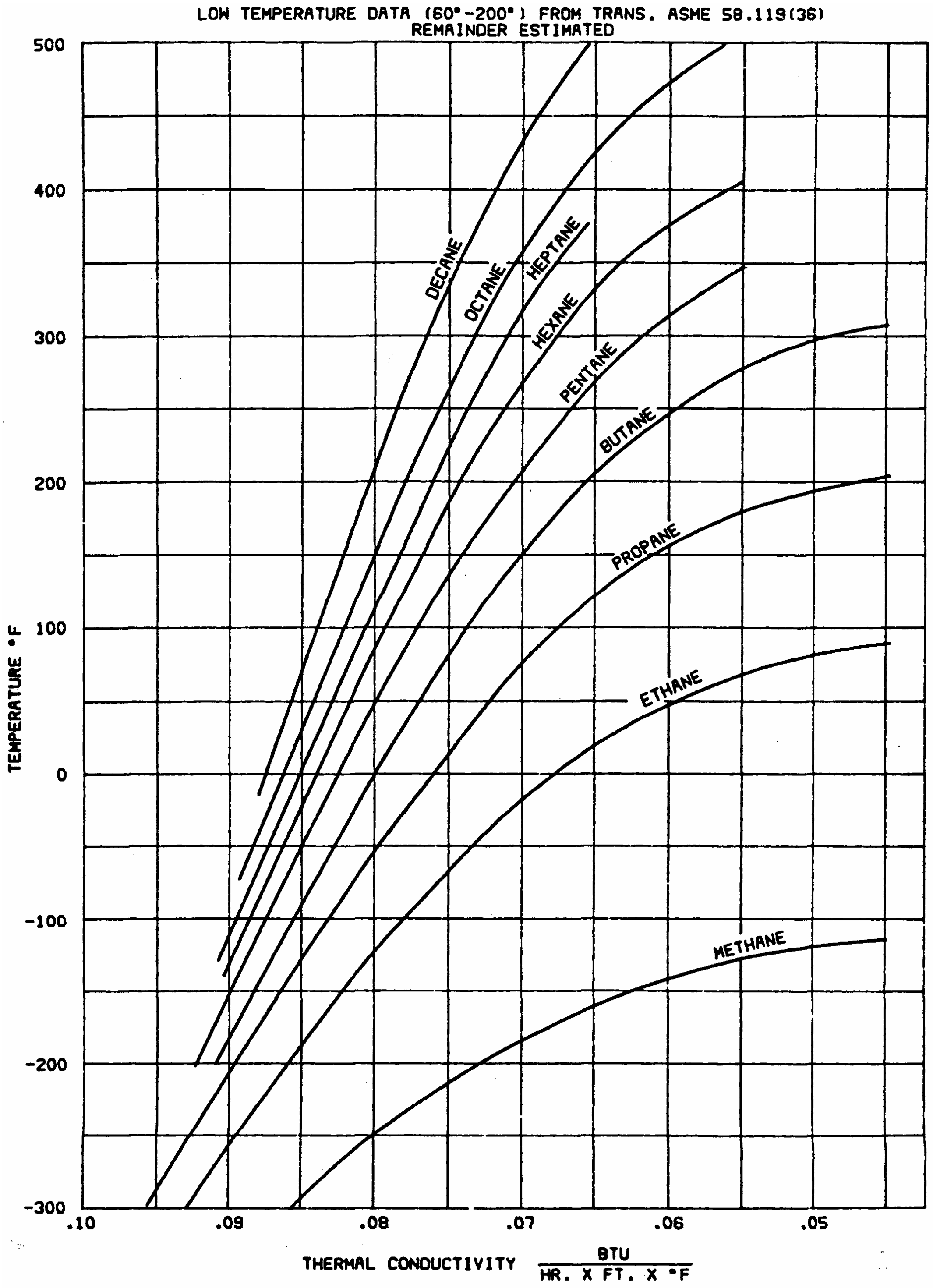


Figure 2.10: Thermal Conductivity of Normal Paraffinic Hydrocarbons

2.6 Thermal Conductivities

Liquids - Hydrocarbon liquids conductivity is given in Figure 2.10. Also some data for H_20 is given in Maxwell, p. 214.

Gases - Maxwell, p. 215 and 216 gives data on miscellaneous gases and hydrocarbon gases vs MW. Also Katz, Figure 4-119, p. 185 gives data at low pressures (also this is given in GPSA Data Book, Fig. 16-29). At high pressures, Lenoir, Junk and Cumming[15], have developed charts similar to that used for viscosity. They give a thermal conductivity ratio vs P_r and T_r where thermal conductivity ratio is:

$$\frac{k \text{ at high pressure}}{k \text{ at atmospheric pressure}} \quad \text{from } 16.29$$

This is shown as Figure 16.31 in the GPSA Data Book.

2.7 Surface Tension

Data on surface tension for hydrocarbons is given in Figure 16-31. (Figure 16-29 in the metric version) of the GPSA Data Book or p. 127 of Katz. In the GPSA Data Book it is calculated from the equation:

Equation 2-47

$$\sigma^{0.25} = \frac{P}{M}\left(d_1 - d_V\right)$$

Where:

ó = surface tension

P = parachor from Figure 16-34

M = molecular weight of compound

d_L = density of liquid at temperature of system

d_V= density of vapour at temperature of system

Also, on P. 16-29 and 16-34 of the GPSA Data Book a method for adjusting for high pressure (Weimag and Katz method) and mixtures is given.

2.8 Molecular Weights of Hydrocarbons (MW)

Sometimes it is desirable to find MW of condensate. This can be done from API gravity and mean average boiling point which is determined from an ASTM distillation. See Figure 16-18 of the GPSA Data Book.

Problems

7. A gas of the composition given below is to be recycled to recover the sulphur, condensate and lpg's. The Energy Resources Conservation Board has stated that 60% of the volume of raw gas removed must be replaced by the recycled sweet pipeline gas produced from a

processing plant that is built for extracting the products produced.

Determine the amount of make-up gas that must be supplied to the facility to handle this requirement or the amount of gas that is available for sale.

Also, determine quantity of sulphur in long tons per day, condensate in barrels per day, butane in barrels per day and propane in barrels per day recovered by the plant.

Data

a) Raw gas flow to the plant is 300 MMSCFD (at 14.4 psia and 60°F as the base measuring condition).

b) The reservoir pressure is 4300 psia - sweet gas must be returned at that pressure.

c) The design plant recovery efficiencies are:

Sulphur	95%
Condensate	100%
Butanes	100%
Propane	85%

d) The fuel gas required for plant operation is equivalent to 2% of the raw gas feed but sweet gas is used.

e) The gas analysis is:

Component	Mole %
N_2	0.50
H_2S	17.06
CO_2	2.94
C_1	57.50
C_2	9.80
C_3	3.94
iC_4	1.06
nC_4	1.96
iC_5	0.74
nC_5	0.90
C_6	0.55
C_7+	3.05

f) The raw gas reservoir temperature is 200°F.

The heating load of a processing plant is made up of 4 furnaces. The process duty on each of the furnaces is as follows. The efficiency of each is also given.

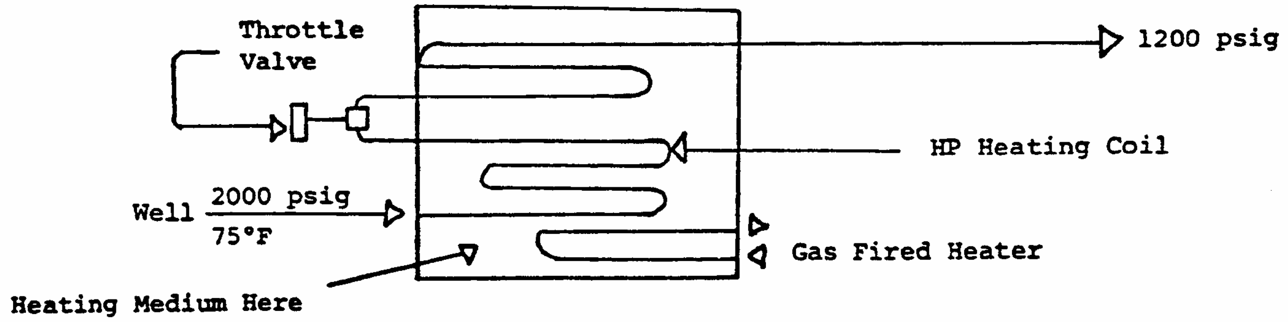
Furnace No.	Process Heating Required BTU/hr	Design Efficiency % *
1	$10x10^6$	70
2	$5x10^6$	65
3	$25x10^6$	75
4	$40x10^6$	75

* Based on Gross Heating Value

Gas is available at $I.25/MMBTU on an interruptable basis and $I.50/MMBTU on a firm basis. The fuel that is used as a standby is n-butane which can be sold for 25¢/US gal when it is not used as fuel.

How many days interruption could the process plant stand per year and still break even if it used interruptable gas instead of firm gas?

A well produces gas at 25 MMSCFD. The wellhead pressure is 2000 psig at this flow rate and it is at 75°F. The gas is delivered from the wellhead through a heater to a pipeline that operates at 1200 psig. You are to determine the heat duty of the high pressure heating coil in BTUs per hour. The sketch below shows the flow scheme.



The gas is sweet and the gravity of the gas is 0.7.

A gas of the following composition is to be processed for ethane and propane plus recovery. The amount of gas that is available is 300 MMSCFD (at 60°F and 14.696 psia). The exit gas from the plant must be returned at 985 BTU 's/SCF as measured by a Thomas Calorimeter.

Component	Mole %
N_2	3.5
C_1	83.2
C_2	10.3
C_3	1.8
iC_4	0.3
nC_4	0.4
C_5+	0.5

Determine the barrels per day of pure ethane that can be removed. Assume that all the C_3+ is removed from the incoming gas during the process. Assume fuel gas is supplied from down stream of plant (i.e. the plant residue gas).

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Reading List

1. R.L. McKee, White, W.E. and Dauber, F.E., "The Des~gn Implication of Equation of State Evaluations", Proceedings 62 Gas Processors Convention, 1983.
2. K.E. Starling, M. Mannan arid J.L. Savidge, "Equation Predicts Supercompressibility For Wet Sour Gas", Oil and Gas Journal, January 2, 1989, p. 31.

3.0 Phase Behaviour of Natural Gas Systems

- What are Phases?
- The Phase Rule, PV, PT and PVT
- Diagrams
- Retrograde Phenomena
- Binary and Complex Systems
- Non-ideal Systems

3.1 What is a Phase?

A single continuous media containing one or more substances in which the relation between temperature, pressure and volume can be expressed by a continuous equation is a phase. Another way is to use the Clausius Clapeyron Equation which explains how a phase is changed. This equation can be expressed as follows:

Equation 3-1

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

where:

ΔV is the change of volume

ΔH is the heat content of the phase change

P is the pressure at the phase change

T is the temperature at the phase change

Thus a phase change occurs when there is a finite change in volume and heat content when the pressure and temperature are constant.

3.2 What are Some Phases and Their Features?

Gases

Distinguishing feature is that it occupies the space of container and it can be compressed easily.

Liquid

It takes the shape of the bottom part of a container. Also it is hard to compress; only under extreme pressure.

Solid

It has definite shape and is not compressible. We can have several liquid and solid phases, however not more than one gas phase. In the gas industry we are lucky in that we only need to consider liquid and gas phases. We do have the special case of elemental sulphur in gases containing amounts of H_2S. This is considered later in this section.

3.3 Why Study About Phases?

We encounter many physical conditions in handling fluids in which two phases are present, i.e.

a) Fluid flow in gathering lines

b) Distillation

c) Absorption

d) Heat transfer operations, i.e. vaporization.

In studying about phases we initially will try to understand visually what happens between phases and later, in another section (Vapour- liquid equilibria) set up mathematical relationships to predict phase conditions.

3.4 History

This is an old subject. Some of the more important pioneers are:

a) Faraday, who in 1845 worked out phase diagrams for substances such as N_2, H_2S, SO_2, CO_2, etc.

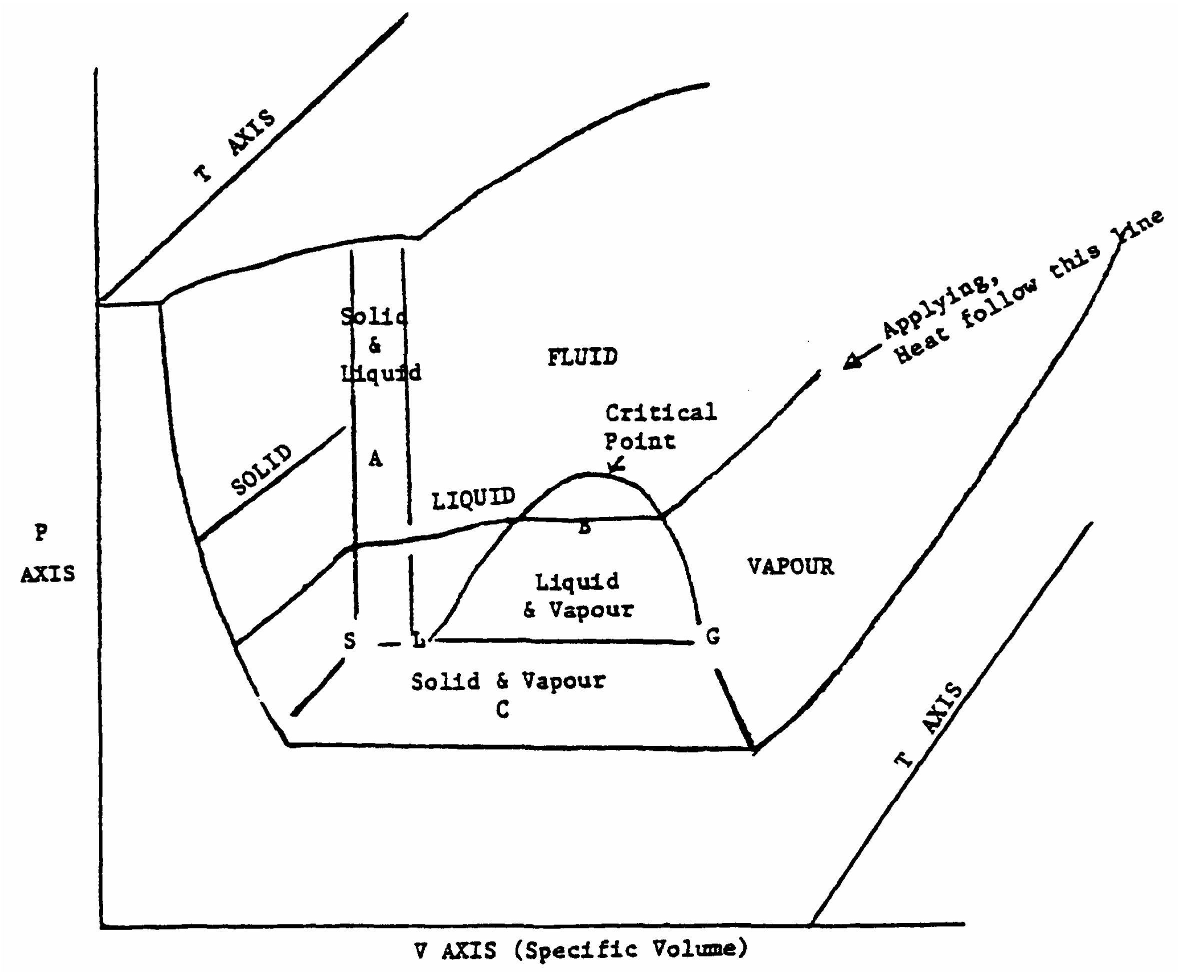
b) Andrew, who in 1869 noted the continuity of gas and liquid phases at high pressures and temperatures. This led to the concept of the critical point.

c) Gibbs, who in 1876 enunciated the phase rule.

d) Kuenen, who in 1892 discovered the retrograde condensation phenomena.

3.5 Single Component Systems

Let us consider a single component, three dimensional diagram. Figure 3.1 represents such a diagram. The diagram shows when a single phase and when two phases are present.



Surface	A Solid and Liquid in equilibrium.
Surface	B Liquid and Vapour in equilibrium.
Surface	C Solid and Vapour in equilibrium.
SLG	Three phases present.

Figure 3.1: Three Dimensional Diagram for a Single Component

Also, the case of three phases present is shown as the line SLG. Let us consider projections of this model onto a two-dimensional surface. We have two normal types of diagrams.

These are:

PT diagrams (Figure 3.2) in which planes of constant volumes are taken.

PV diagrams (Figure 3.3) in which various lines of constant temperature are taken.

Note: V is specific volume (i.e. volume of one unit of Mass).

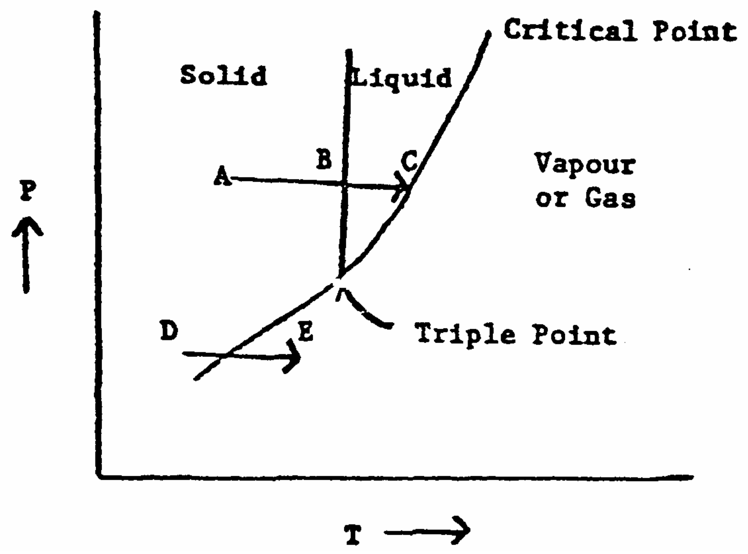


Figure 3.2: PT Diagram - Single Component

When going from A to B to C the phases are Solid, Liquid, Gas. When going from D to E the phases are Solid - Gas. Some examples of solid, gas systems are:

$AlCl_3$

Phthalic anhydride

Iodine

CO_2

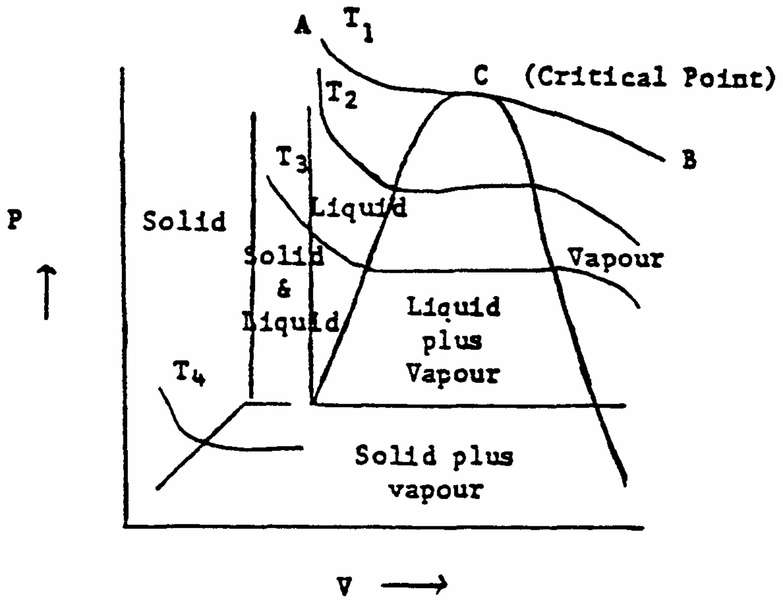


Figure 3.3: PV Diagram - Single Component

- If we follow T_1 there is no change of phase.
- If we follow T_2 we go from liquid to liquid plus vapour to finally vapour.

- If we follow T_3 we go from solid to solid plus liquid to liquid plus vapour to vapour.
- If we follow T_4 we go from solid to solid plus vapour to vapour.

Also consider the conditions of vessel containing a certain weight of material with temperature T_3. It would contain liquid of specific volume, b, and vapour of specific volume, a.

Note: lines of constant temperature are called isotherms.

3.6 Critical Points

Please refer to the PV diagram (**Error! Reference source not found.**). When reducing the pressure along the curve ACB no change of phase occurs. Also, you remember that in Figure 3.2 the liquid vapour line stopped at a high pressure and temperature.

The point C in PV diagram and the top point on the liquid vapour line in PT diagram is called the critical point. It is the unique point for substance where the liquid and gas phase become identical.

Each individual substance has a definite critical temperature and critical pressure. There is also a critical temperature and pressure for mixture which will be discussed later.

Here are some data on common critical points. Also, the boiling point is given:

Table 3.1: Critical Data (Imperial)

	Critical Pressure lb/in2 abs	Critical Temperature °R	Boiling Point °F
Methane	668	343	-259
Ethane	708	590	-127
Propane	616	666	-44
i Butane	529	735	11
n Butane	551	766	31
i Pentane	490	829	82
n Pentane	489	846	97
n Hexane	437	914	156
n Heptane	397	973	209
n Octane	361	1024	258
Carbon dioxide	1071	548	-109
Hydrogen Sulphide	1306	673	-77
Nitrogen	493	228	-320

Table 3.2: Critical Data (Metric)

	Critical Pressure kPa	Critical Temperature °K	Boiling Point °C
Methane	4605	190.5	-161.5
Ethane	4881	305.3	-88.6
Propane	4247	369.8	-42.1
i Butane	3647	408.0	-11.7
n Butane	3799	425.0	-0.5
i Pentane	3378	460.8	27.9

n Pentane	3371	469.6	36.1
n Hexane	30 13	507.7	68.7
n Heptane	2737	540.0	98.4
n Octane	2487	569.2	125.7
Carbon dioxide	7384	304.0	78.2
Hydrogen Sulphide	9004	373.0	-60
Nitrogen	3399	120.5	-195.3

Note: The boiling point is the temperature at which the vapour and liquid phases are in equilibrium when the vapour pressure is one atmosphere.

3.7 Vapour Pressure

In Figure 3.2 the line between surfaces B and C is the vapour pressure curve and gives the pressure of single component above a pure liquid of that component at the temperature specified.

3.8 Summary - Single Component

a) A functional relationship of the form

Equation 3-2

$$f(P,T,V) = 0$$

exists for single component systems. The surface which this relationship describes has dis continuities in it because of the existence of vapour-liquid, solid-liquid, and solid-vapour equilibrium.

b) The triple point is the unique pressure and temperature where solid, liquid and vapour can all exist in equilibrium for a single component system.

c) The critical point is the unique condition where the properties of the liquid and vapour phases become identical.

d) The salient features of the P-V-T surface may be conveniently projected onto P-T and P-V planes to facilitate both qualitative and quantitative representation.

e) An isotherm represents the intersection between the P-V-T surface and an isothermal plane.

f) The boiling point of a pure material is the temperature where the vapour pressure is one atmosphere.

g) The vapour pressure of a material is the pressure where two or more phases may co-exist at any fixed temperature.

h) The terms liquid, vapour and solid lose their significance unless at least two phases are present.

3.9 The Phase Rule

Before proceeding to more complicated systems we should review the phase rule which Gibbs first enunciated in 1876. This rule applies to systems in equilibrium and states that the number of components plus 2 equal the number of phases plus the degrees of freedom (or the number of independent variables to determine the system)

$C + 2 = P + F$

Where:

C = components

P = number of phases

F = number of degrees of freedom or number of variables required-to determine-system.

Some examples are:

a) For water boiling (two phases present)

$1 + 2 = 2 + F$

Thus it is necessary to specify a variable such as temperature or pressure to define the system. Thus by specifying different temperatures a vapour pressure curve can be determined.

b) For a system of methane and ethane as a liquid, three degrees of freedom are needed to define the system.

$2 + 2 = I + F$

$F = 3$

Thus you have to specify the pressure, temperature and the composition of the solution to define the system.

3.10 Systems of More Than One Component

A qualitative study of the phase behaviour of single component systems has revealed all of the essential features which are encountered even in complex systems. The concept of two or more phases co-existing, of vapour pressure, of the critical point, and of a continuous single phase fluid region is applicable to any system regardless of its complexity. The fundamental difference between single component systems and complex systems is that every time we add one more component we gain one additional degree of freedom. That is we may arbitrarily specify one additional variable and for a binary system, the functional relationship becomes:

$$f(P,T,V,X) = 0$$

where:

X is the composition.

It is obvious from this relation that a three dimensional model can no longer be used to pictorially represent the complete behaviour of even a vinary system. Any three dimensional representation of the behaviour of a system containing more than one component will of necessity be capable of showing the values of only three of the possible variables. The choice is arbitrary, but the most common practice is to select pressure, temperature, and composition. Every point represented on such a diagram will have a particular specific volume associated with it, as determined by the functional relationship above, but the coordinates of volume will not be represented on the diagram.

Figure 3.4 shows a schematic representation of the P-T-X behaviour of a typical binary system including part of the vapour-liquid equilibrium region. The region of solid formation has been excluded because of the complexity of the diagram and because it is seldom pertinent in gas processing studies.

The characteristic features of the diagram are somewhat more difficult to visualize than they were in the P-V-T diagram for a single component. This is because the only lines one sees in space are those formed when two surfaces intersect non-tangentially. On a P-V-T surface this occurs every time the single phase region intersects a two phase region, but on a P-T-X diagram it never occurs at pressures and temperatures in the vapour liquid region. It will be appreciated that the additional degree of freedom means that what were points for one component are lines for two components; what were lines have become surfaces; and what were surfaces have become volumes. In this way the saturated liquid line of Figure 3.3 has

become a saturated liquid surface M in Figure 3.4 and the saturated vapour line has become a saturated vapour surface N. These two surfaces, commonly called the bubble point surface and the dew point surface, form the upper and lower boundaries of a vapour-liquid volume. This two-phase volume is terminated at the left side of the figure by the vapour pressure curve of pure A denoted by the line 6-7. (It will be noted that since volume has been omitted in this diagram, the curve 6-7 is really the projection of the vapour liquid surface for A as seen in Figure 3.1) . Similarily, the vapour pressure curve 8-9 for pure B terminates the region at the right side of the diagram.

The critical point has become a critical line or critical locus for the binary system. This locus, indicated by 7-10-9, terminates the bubble and dew point surfaces at the high temperature side of the diagram.

The diagram is terminated on the P-x plane by an arbitrarily isothermal plane which leaves its trace 6-11-8 on the bubble point surface and 6-12-8 on the dew point surface.

Let us consider PT diagrams. Figure 3.5 on P. 14 shows the diagram for a two component system with only liquid and vapour present.

Figure 3.6 is the PT phase diagram for a mixture of a fixed composition. In this figure let us consider going from point 1 to point 4 by increasing the pressure. At point 2 condensation starts (dew point). It continues until point 3 is reached where total condensation is experienced (bubble point), then to 4.

Another useful diagram is the TX diagram (Figure 3.7), i.e. where the pressure is constant.

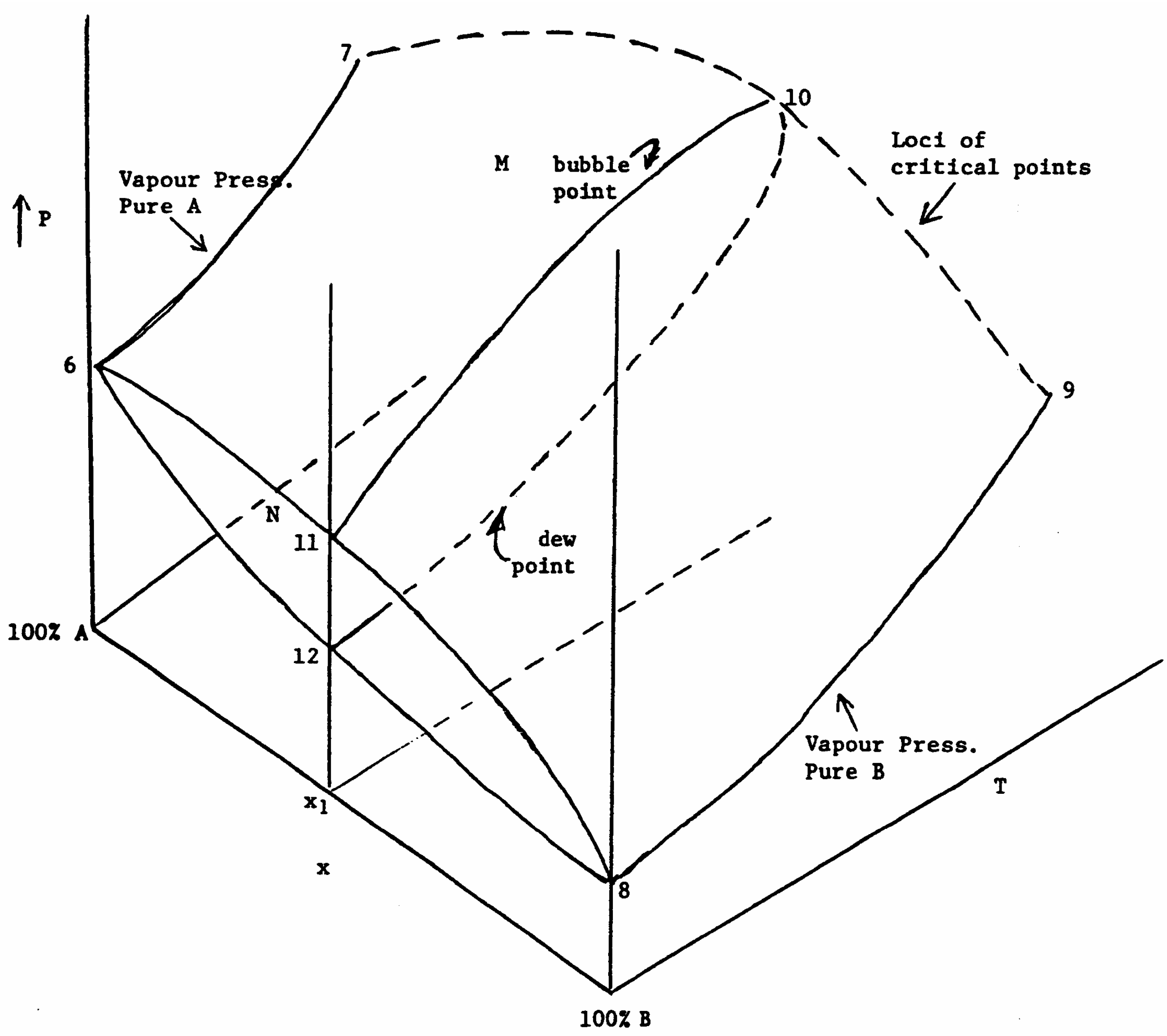


Figure 3.4: Schematic Representation of P-T-x Behavior of a Typical Binary System

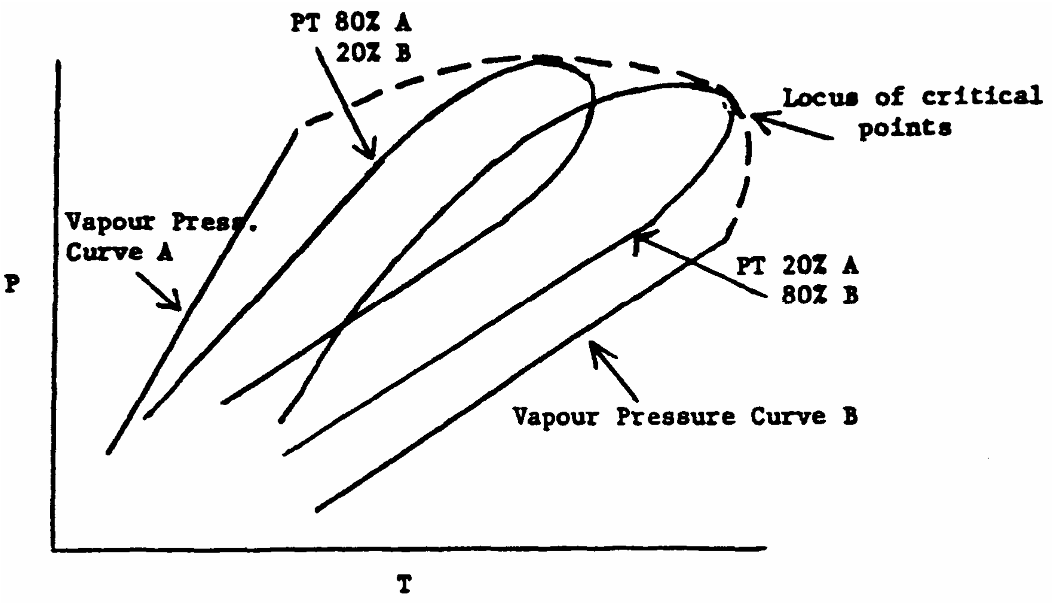


Figure 3.5: PT Diagram - Two Components (A & B), Different Composition

A PT diagram for constant composition can be shown as:

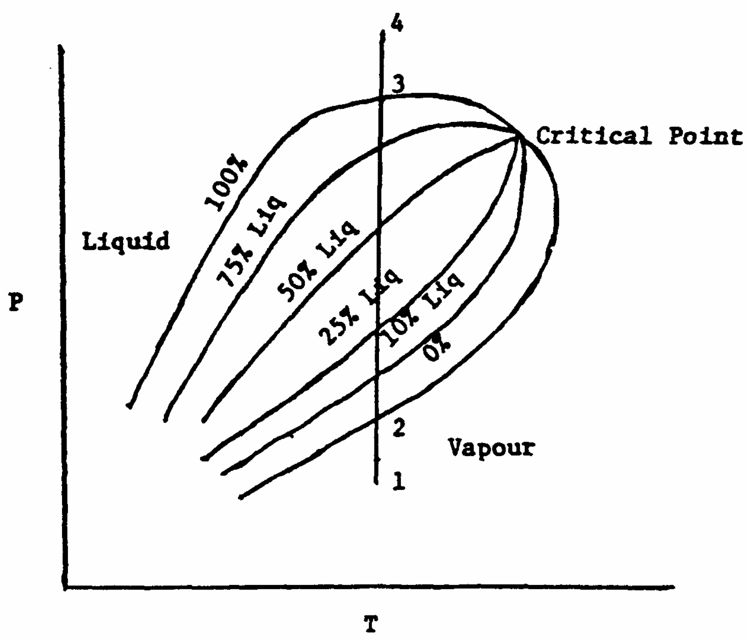


Figure 3.6: PT Diagram - Two Components, Constant Composition

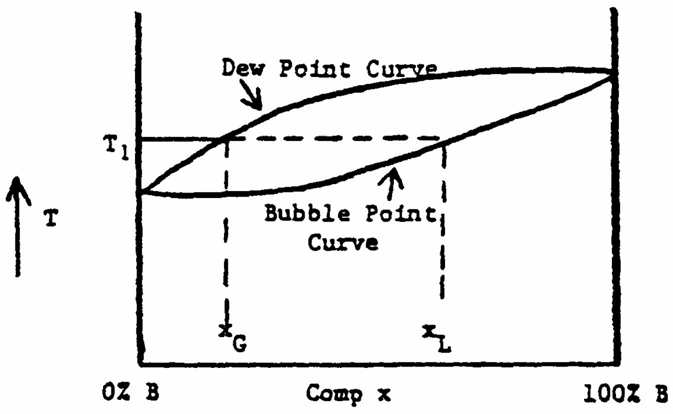


Figure 3.7: Temperature Composition Diagram

In Figure 3.7 the top curve is the composition of the vapour and bottom curve is composition of liquid. At temperature T_1 the gas composition is x_G and the liquid composition is x_L . This shows how two components can be separated by distillation.

We also have a useful representation by the composition diagram with P and T constant. This is shown in Figure 3.8.

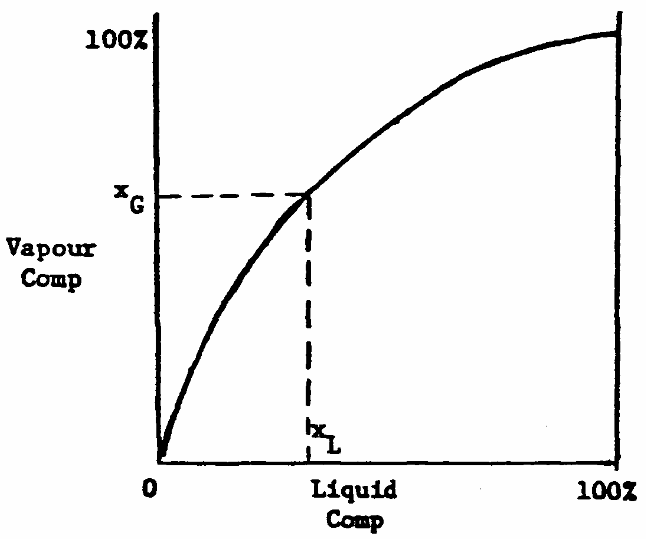


Figure 3.8: Vapour Liquid Composition Diagram

This figure is also important in distillation.

Please note that Figures 3.7 and 3.8 are for ideal solutions. When non—ideal solutions occur, such conditions as maximum or minimum boiling point for mixtures occur. For example Figure 3.9 shows a temperature composition for a minimum boiling point separation.

Also note that the critical point for a binary system is not necessarily the highest temperature or pressure where two phases can exist together for any composition. The critical point is formed by the intersection of the dew point and bubble point surfaces. The highest pressure at which two phases can exist together is the *cricondenbar* and the maximum temperature at which two phases exist is the *cricondentherm*.

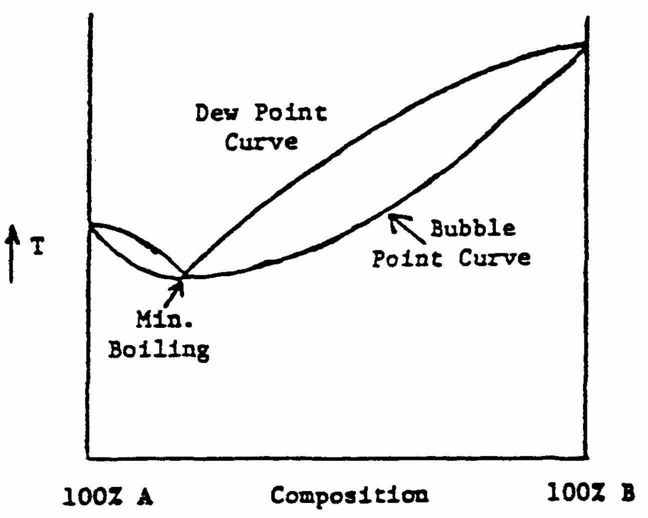


Figure 3.9: Non-ideal Temperature Composition Diagram

3.11 Definitions

Before considering further multi-component systems, let us consider a few definitions. These are:

Bubble Point

This is defined as the temperature at which the first sign of vapour appears. It varies, of course, with pressure and is the same as the boiling point for a single component system at pressure of the system.

Dew Point

This is defined as the temperature at which condensing takes place. This varies with pressure.

With a pure substance the bubble point and dew point are the same, but not so with a mixture. i.e. Take a mixture of

Methane	20%
Ethane	20%
Propane	20%
Isobutane	10%
Butane	10%
Pentane	20%

If the bubble point is determined it will be close to the boiling point of methane at the pressure of the system, while the dew point will be closer to the boiling point of pentane at the pressure of the system. For a system to totally condense it is at its bubble point and for a system to totally evaporate the system has to be at its dew point.

3.12 Multicomponent Systems

It is not possible to graphically represent the detailed behaviour of systems containing more than three components. However, the essential features may be depicted for systems of a fixed composition on P-T coordinates, much as in the case of a binary system; or in the case of systems of variable composition, on a ternary diagram using pseudo pure components, that is, components made up of mixtures of selected components from a complex system. For example, for a system containing C_1 to C_5, one component could be C_1, one could be C_2 and C_3, and the third could be C_4 and C_5. For obvious reasons, this latter technique is not rigorous, but nevertheless it is sometimes useful for a qualitative description of certain phase behaviour phenomena.

Figure 3.10 is an important diagram which depicts a multi—component system with a fixed composition.

Normally, on increasing the temperature of a liquid at constant pressure from A to D the bubble point is reached first then vapourization continues with increasing amounts being formed until 100% vapour is formed at C. At constant temperature, on decreasing the pressure from B to E, a continuing increased amount of vapour is formed.

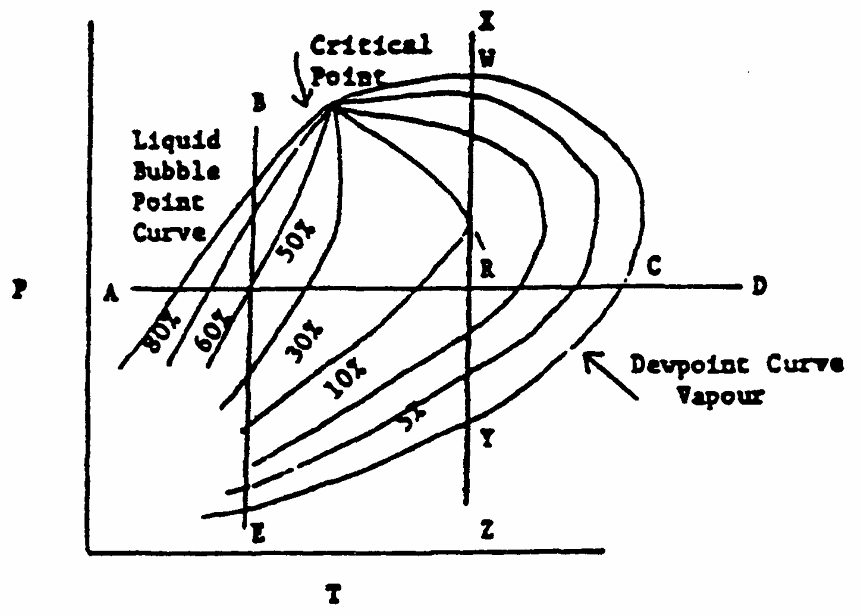


Figure 3.10: Retrograde Phenomena I

3.13 Retrograde Phenomena

Let us next consider the case in **Error! Reference source not found.**, when the pressure is reduced from point X to point Z. At W liquid begins to form on pressure reduction and continues until R is reached where the maximum amount of liquid is developed, approximately 30%, then a continued reduction of pressure causes the liquid to vapourize until the point Y is reached when a 100% vapour again occurs. This phenomena is retrograde condensation and is particularly important in natural gas reservoirs, as most higher pressure gas rich reservoirs exhibit this phenomena. Thus liquids will drop out in the reservoir when the pressure is decreased and may be lost. These liquids may be re-evaporated by dry gas if a cycling scheme is used. Havlena[1] et al, discuss this in some detail.

The reverse of the above procedure, i.e. going from Z to X, is called retrograde evaporation.

Another phenomenon is, if the pressure reduction hits right at the critical temperature of the mixture, then at that point 50% of the fluid liquefies and then progressively evaporates.

Also, if the critical point is located as in Figure 3.11, between R and C an increase of temperature at constant pressure can cause liquid to drop out. This is called isobaric retrograde condensation.

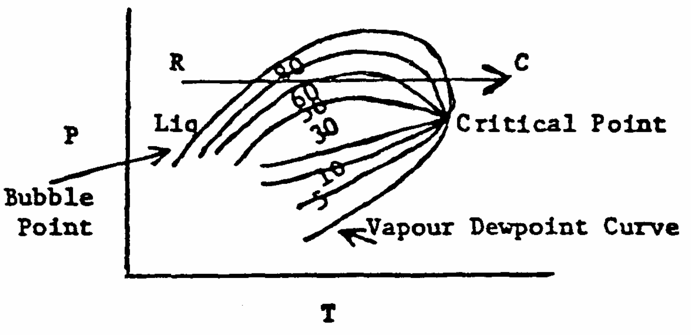


Figure 3.11: Retrograde Phenomena II

3.14 Typical Reservoirs

Let us look at the phase envelopes of various types of reservoirs.

- a) Crude Oil
- b) Dry Gas
- c) Wet Gas
- d) Condensate

In the following Figures T_F is the reservoir temperature and T_S is the separator temperature. P_F is the initial reservoir pressure.

3.14.1 Oil Reservoir

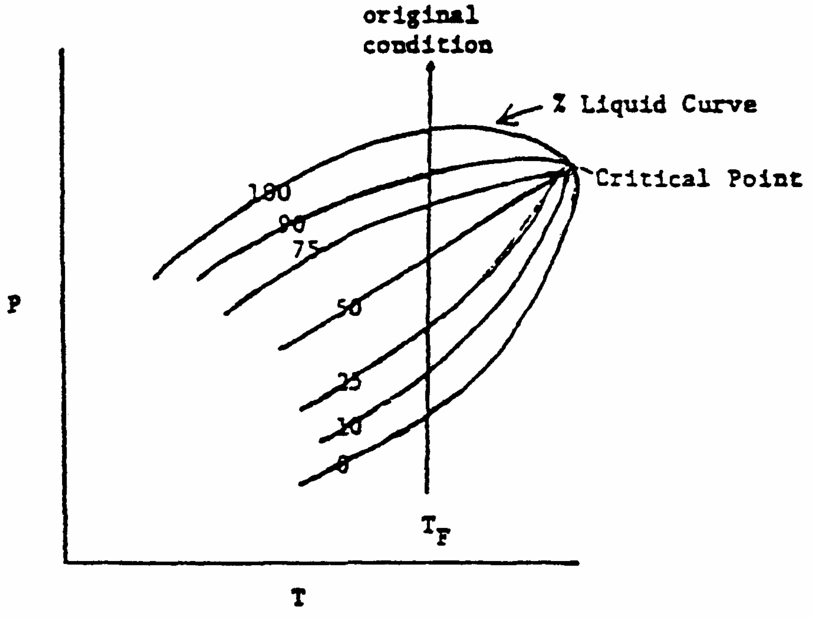


Figure 3.12: Oil Reservoir Phase Envelope

Reservoir temperature is less than critical. As pressure decreases during production, gas forms and continues to form.

3.14.2 Dry Gas Reservoir

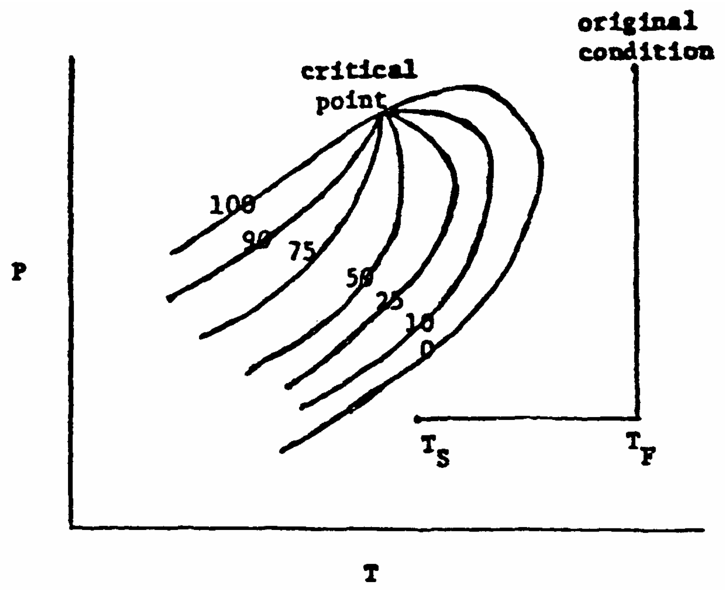


Figure 3.13: Dry Gas Reservoir Phase Envelope

In this case, as the pressure is decreased no condensation occurs. The reservoir temperature is well above the critical. Even when the temperature is reduced to that at the separator because of the Joule- Thompson effect, no condensation occurs.

3.14.3 Wet Gas Reservoir

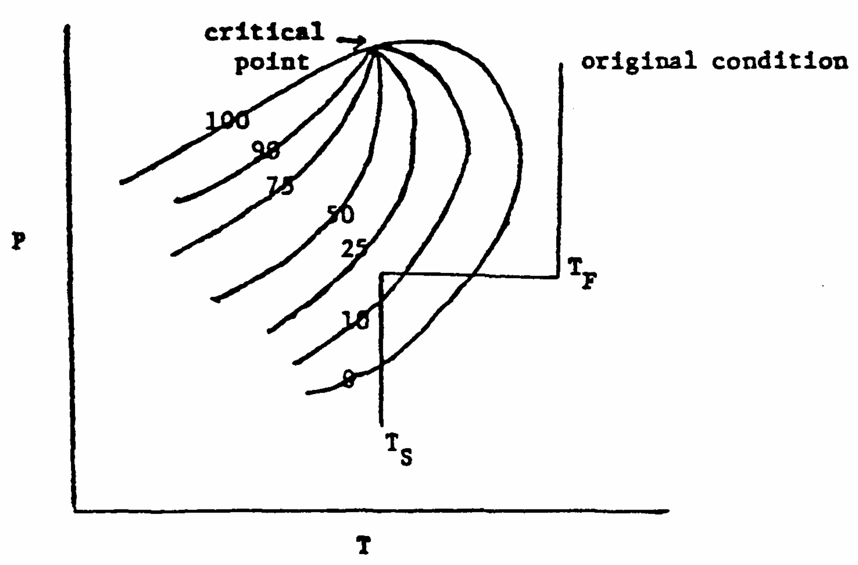


Figure 3.14: Wet Gas Reservoir Phase Envelope

This is the same as a dry gas, except that the separator temperature goes into the two phase region and liquid drops out.

3.14.4 Condensate Reservoir

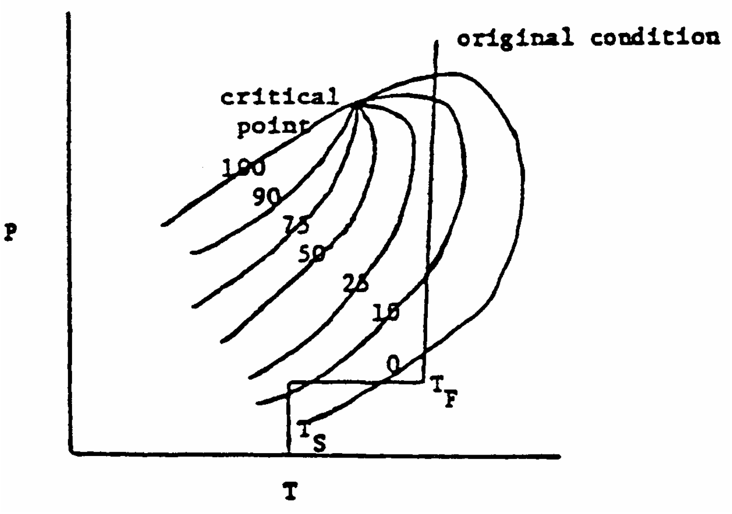


Figure 3.15: Condensate Reservoir Phase Envelope

The reservoir temperature is between critical and cricondentherm. The reservoir will sometime in its life be in the two phase region. Condensate will also normally exist in the separator.

3.15 Ideal Systems

We have discussed primarily ideal systems, particularly ideal solutions. In general, the following principles have been followed:

a) Ideal Gas Law PV = RT

b) Dalton Law of Partial Pressure, partial pressure component A = (mole fraction of A in vapour) (Total Pressure)

c) Ideal Solution. Volume of solution of a mixture is equal to the sum of the volume of each individual component.

With hydrocarbons the ideal solution principle is generally followed; however, when a non—hydrocarbon is present, such as CO_2,

two liquid phases can be formed. Also we can get both maximum and minimum boiling points, etc.

3.16 The Sulphur / H_2S System

A special case of phase behaviour occurs in gas systems in which there is a very high concentration of H_2S at high pressures. The problem that occurs is that at high pressures and temperatures gas containing high percentages of H_2S seem to dissolve elemental sulphur. The well known work of D.R. Weiland[2] reports on this. Figure 3.16 shows some data for

50% H_2S. It shows that as the temperature and pressure increase, more sulphur is dissolved. Therefore, when the gas is produced out of a reservoir and the pressure and temperature are dropped, elemental sulphur is precipitated out. This elemental sulphur plugs the well tubing and gathering lines. J.B. Hyne[3] has made a study of sour gas reservoirs in Alberta to see when the problem of deposition occurs and what causes it. He found that with high H_2S wet gas streams (i.e. those containing a lot of condensate) deposition did not occur, as the condensate seems to dissolve the deposited sulphur. He developed a correlation that indicated the probability of deposition. This is given in Figure 3.17[5]. This correlation plots the wellhead temperature times the wellhead pressure and $\left[1+C_5^+\%\right]$ of the gas versus the formation temperature and pressure. Probably at high pressure H_2S forms polysulphides which disassociate on reducing pressure to H_2S and elemental sulphur according to the reaction

$$H_2S_x = S_{x-1} + H_2S$$

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1. Z.R. Havlena, J.D. Griffiths, R. Pot and O.G. Kiel, "Canadians Cycle Condensate, Reservoir and Pressure Decline Studies", Oil & Gas Journal, June 10, 1968, p. 89.
2. D.R. Welland, Ph.D. Dissertation, Texas A & M, 1958. Also presented to the Society of Petroleum Engineering, Oct. 4— 9, 1959.
3. J.B. Hyne, "Study Aids Prediction of Sulfur Deposition in Sour Gas Wells", Oil and Gas Journal, Nov. 25, 1968, p. 107.
4. J.B. Hyne and E.F. Muller, "The Sulphur/Hydrogen Sulphide System", Paper presented to the 19th Canadian Chemical Engineering Conference and 3rd symposium on Catalysis, Edmonton, Alberta, October 19, 1969.
5. R.A. Tomcej, H. Katra and B. Hunter, Paper 88—39—4 at 39th Annual Meeting of the Petroleum Society of the CIM (1989).

Reading List

1. O.R. Schweitzer and C.E. Wales, "Phase Rule and Equilibria Relations", Chemical Engineering, May 27, 1963, p. 117.
2. J.H. Erbar and R.N. Maddox, "Hydrocarbon—Systems Phase Behaviour", Oil and Gas Journal, January 19, 1981, p. 68.

4.0 Vapour Liquid Equilibrium Data and Computations

- Importance of vapour liquid equilibrium data
- K factors
- Convergence pressures
- Calculation of dew and bubble – points
- Equilibrium flash calculations

4.1 Introduction

The natural gas industry is fortunate in that there is published a great deal of data on physical properties, including vapour liquid equilibrium constants. We use vapour liquid equilibrium data for:

1. Reservoir calculations.
2. Two phase pipeline flow calculations.
3. Inlet separation calculations.
4. Distillation calculations.
5. Absorption calculations.
6. Tower pressure calculations.
7. Refrigeration calculations.

We are very fortunate as compared to crude oil systems which do not have equilibrium data for individual components but have to use correlations depending on average boiling point, characterization factor, etc.

4.2 Equilibrium Constants

What is the equilibrium constant? It is defined as "K" where

Equation 4-1

$$K_i = \frac{y_i}{x_i}$$

where:

y_i = mole fraction of component "i" in gas phase.

x_i = mole fraction component "i" in the liquid phase.

4.3 Ideal Equilibrium Ratio

4.3.1 Raoult Law

For an ideal gas and liquid the following equation applies:

Equation 4-2

$$P_i = P_{VPi}\, x_i$$

This states that the partial pressure of a component above a solution is equal to the vapour pressure at temperature and pressure of system for the pure component times the mole fraction of "i" in the liquid.

4.3.2 Dalton's Law

Equation 4-3

$$P_i = P_t\, y_i$$

Partial pressure of component "i" in system = mole fraction of "i" in the gas times total pressure of system.

Combining the above equations

Equation 4-4

$$y_i P_t = P_{VPi}\, x_i$$

or

Equation 4-5

$$\frac{y_i}{x_i} = \frac{P_{VPi}}{P_t}$$

or as we have defined

Equation 4-6

$$K_i = \frac{y_i}{x_i} = \frac{P_{VPi}}{P_t}$$

The above equation is restricted to substances at low pressures, a long way from the critical pressure, that obey the ideal gas and ideal solution laws.

4.4 Modifications of Ideal Equilibrium Patios

The previous K value is based on both ideal gas and ideal solution laws. We can extend the application of calculated K to higher pressures by use of the term fugacity "f". This is sort of an ideal vapour pressure. i.e. the fugacity = the vapour pressure when the vapour behaves as an ideal gas. It can be defined by the equation:

Equation 4-7

$$RT\, d\ell nf = VdP$$

and $f^\circ = P^\circ$ when P° approaches 0.

Now, from the above equation it can be developed that

Equation 4-8

$$\ln \frac{f}{P} = \frac{1}{RT} \int_0^P vdP$$

This applies for gases. For liquids a similar type of equation can be developed using the difference between the actual change in volume and the change in volume of an ideal solution. If there is no difference the fugacity is equal to fugacity of the pure component times the mole fraction. Using fugacities and assuming ideal solutions we have:

Equation 4-9

$$f_i^v = y_i\, f_{vi}$$

where f_{vi} is the fugacity of the component "i" as a vapour at the pressure and temperature of the equilibrium system. (i.e. pure i). Similarly a Raoult Law type of equation can be developed:

Equation 4-10

$$f_i^l = x_i\, f_{li}$$

$f_{\ell i}$ is the fugacity of component "i" as a liquid at the temperature and pressure of the system. (i.e. pure "i").

Now for the equilibrium

$$f_i^v = f_i^l$$

Equation 4-11

$$K_i = \frac{y_i}{x_i} = \frac{f_{li}}{f_{vi}}$$

If non-ideal solutions are experienced activity coefficients γ_i^L which are a measure of the deviation from ideal solution have to be introduced and Equation 11 becomes

Equation 4-12

$$K_i = \frac{y_i}{x_i} = \frac{\chi_i^L\, f_{li}}{\chi_i^V\, f_{vi}}$$

4.5 Actual "K's"

The above ways of calculating "K" are satisfactory part of the time but not always, particula~zly as systems approach critical conditions. Figure 4.1 shows how the K values vary depending on how they are determined. It should be noted how the actual "K" converges to 1 at high pressure. This is called the convergence pressure.

4.6 Measurement of Actual "K's"

Actual K's are determined by taking a mixture of pure compounds, subjecting them to various pressures and temperatures in special cells and determining by proper sampling procedures the composition in the liquid and gas phases. Sage and Lacey at Cal. Tech. pioneered a great deal of this work. Many others such as Kobayshi. at Rice University and Robinson at the University of Alberta have continued this work. From these measurements and by calculations an extensive set of K values for methane to Decane, H_2S, and some other components have been published in the GPSA Data Book.

Also given in this manual are K values for various oils as a function of their boiling point. In the literature there are data for many systems -benzene, toluene, etc., also many chemical systems.

The K values as plotted in the GPSA Data Book are given for various convergence pressures. That is the pressure at which for this set of data all values of "K" converge to one. This applies for any temperature and for each component.

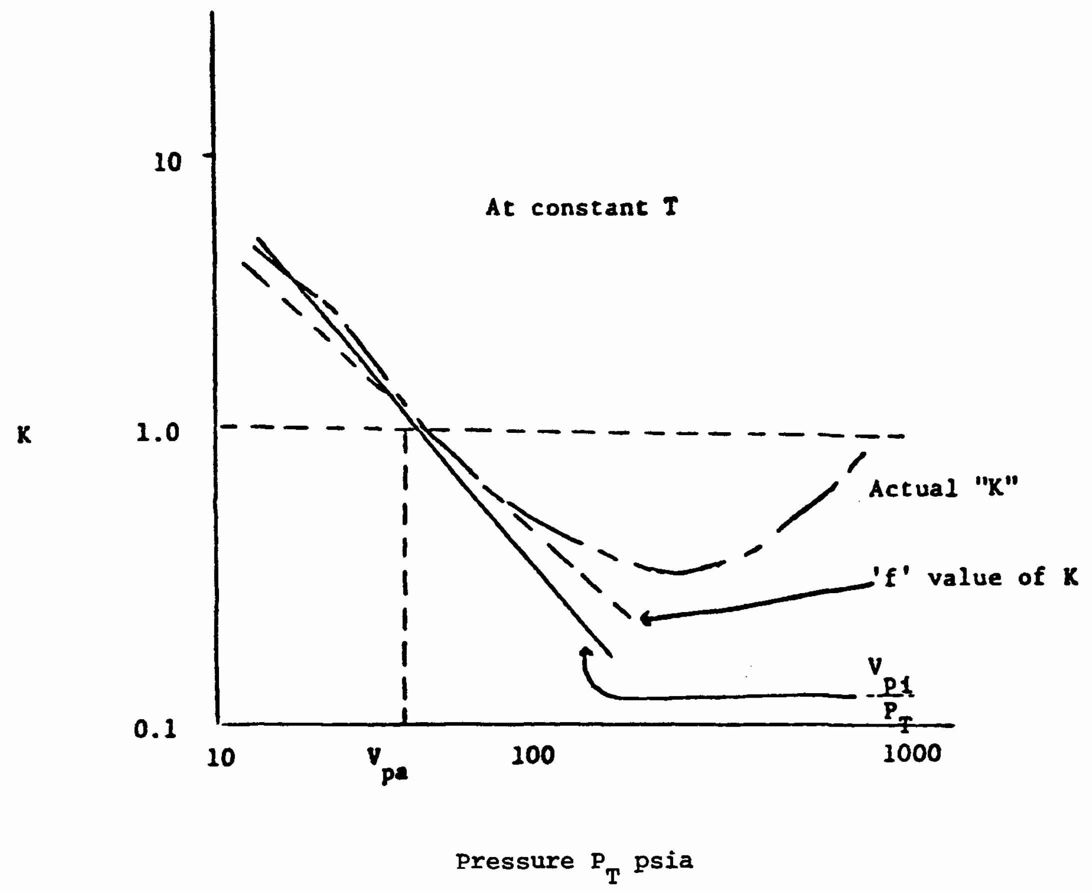

Figure 4.1: Comparison of "K's"

4.7 Methods of Determining "K"

There are several methods for determining "K". The three major methods are as follows: (Starling, Bono, Carnahan and Kwok[1] give a good discussion of these methods).

a) An equation of state for both the vapour and liquid phase -primarily the BWR (Benedict, Webb, Rubin[2]) equation and its modification by Starling[15] is used for this although the Redlich, Kwong[3] equation can also be used.

b) An equation of state can be used for the vapour and a liquid theory equation used for the liquid. Prime example is the Chao, Seader[4] and the Prausnitz Chueh[12] and the Soave[18] methods for calculating "K".

c) A graphical correlation like the GPSA Data Book along with the proper convergence pressure. The Haddon and Grayson[5] data used by the API are also of this type of approach.

We will start with a discussion of the c) approach first.

4.8 Convergence Pressure

To consider method c) as given above we must consider the convergence pressure. At the critical pressure and critical temperature of system "K" must equal 1.0 for all components, since we no longer have two phases but we have a single. phase. For a binary system we can see this effect if we plot K versus the pressure at a constant temperature as shown in Figure 4.2.

For two phases to exist the heavier phases' "K" must be less than one and lighter phases' "K" must be greater than 1. Thus it can be seen that convergence pressure is the critical pressure of a binary and that it has for its critical temperature the temperature in question. The concept of convergence pressure is used as a means of correlating K data. It is calculated primarily from the composition of the system. The effect of convergence pressure selection can be seen from Figure 4.3. As can be seen at low pressure the selection of the convergence pressure is not important. At 150 psia the K values are all the same. At 500 psia K = .64 for an 800 cony, pressure and .48 for a 5000 cony, pressure. At 1000 psia K = 1 for 800 and 1000 cony, pressure and .37 for 5000 cony. pressure.

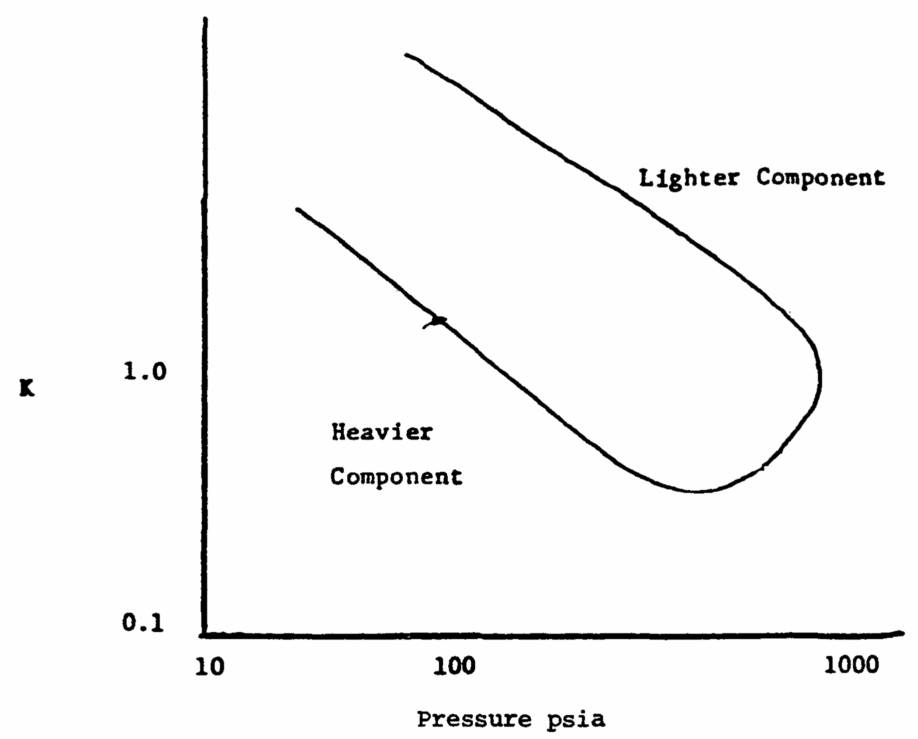

Figure 4.2: Binary System "K's"

As was stated the convergence pressure is a means of correlating K data for a particular composition.

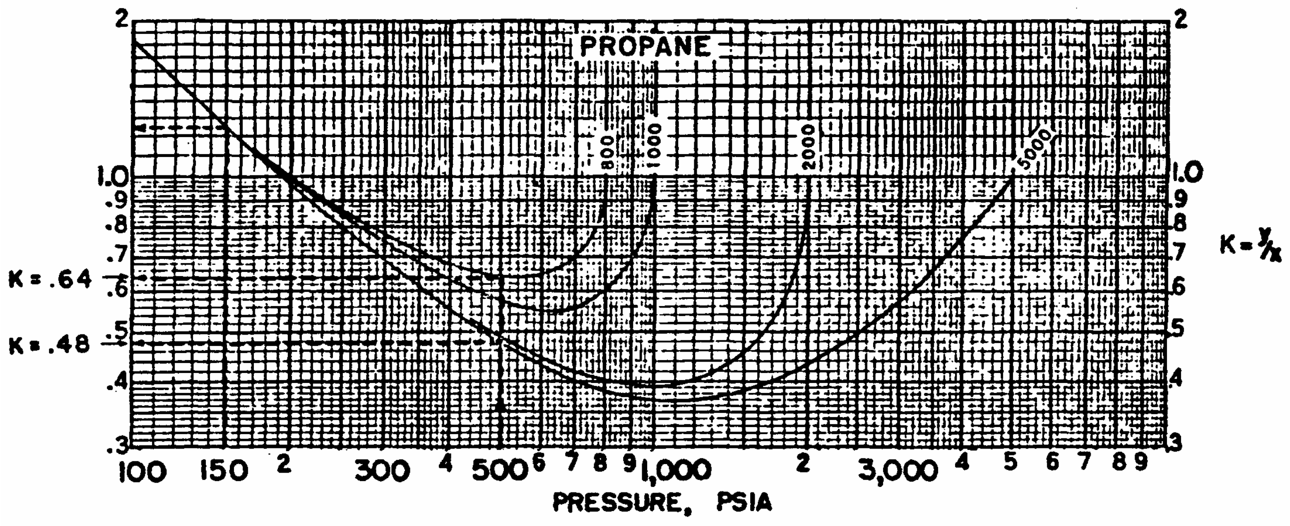

Figure 4.3: Effect of Convergence Pressure on "K's"

In general we can say the equilibrium constant is a function of pressure, temperature and composition or

Equation 4-13

$$K = \phi\left(P, T, x_1, x_2, ...x_n\right)$$

Applying the phase rule for a two phase system the number of independent variables to determine K can be expressed by

Equation 4-14

$$K = \phi'(P, T, x_1, x_2, \ldots\ldots\ldots\ldots\ldots x_{n-2})$$

Now let

Equation 4-15

$$P_K = \phi''(T, x_1, x_2, \ldots\ldots\ldots\ldots x_{n-2})$$

(P_K = Conv. Press.)

Therefore

Equation 4-16

$$K = \phi''(P, P_K)$$

For a binary system

Equation 4-17

$$P_K = \phi^{IV}(T)$$

Equation 4-18

$$K = \phi^{V}(P, T)$$

Thus for a binary system P_K is independent of the composition (or independent of the lightest component).

4.9 How to Find The Convergence Pressures

d) At relatively low pressure, i.e. $\dfrac{P}{P_K} < 0.5$

The chart on Page 18-5 of the GPSA Data Book can be used for this. The method is to take as the lightest component present in any significant quantity (1.0% or greater in a raw mixture; it is usually methane) as the light component of a two component system. The heavy component is estimated from the composition of the remaining components. A visual estimate is usually good enough. Join the heavy and light component together as shown on the Figure and read off P_K against operating temperature.

e) At conditions of $\dfrac{P}{P_1} < 0.5$ there are several methods.

The method given below is probably satisfactory.

For natural gas systems it has been found that the convergence pressure is a function of temperature and the composition of the liquid phase. Hence, if the liquid phase composition is known, the convergence pressure is found by the step-wise procedure listed below.

If the liquid phase composition is unknown, it has to be assumed (estimated) and subsequently checked.

1. Identify the lightest hydrocarbon component which is present at a concentration of at least 0.1% in the liquid phase.
2. Calculate the mass average critical temperature and critical pressure for the remaining heavier components to form a pseudo binary system. (A shortcut approach good for most hydrocarbon systems is to calculate the weight average T_c only.)
3. Trace the critical locus of the binary consisting of the light component and pseudo heavy component. When the averaged pseudo heavy component is between two real hydrocarbons, an interpolation of the two critical loci must be made.
4. Read the convergence pressure (ordinate) at the system temperature (abscissa) from Figure.
5. Using the convergence pressure determined in Step 4 together with the system temperature and system pressure, obtain K-values for the components from the appropriate convergence pressure K-charts.
6. If the liquid composition was initially assumed, calculate it using the K values and overall system composition.
7. If the differences between the assumed and calculated compositions are significant, repeat the entire procedure.

These are other methods.

- Haddon and Grayson5
- Winn
- Lenoir and White

Method of Haddon and Grayson[1]

1. Run a flash calculation at an assumed P_K.
2. Divide liquid into two components.
   a) Lightest component greater than 1.0% (moles).
   b) Rest of components.
3. Calculate critical temperature of pseudo heavy components by any method. Straight mole % can be used and then join the light and heavy components together in the form as given in figure on Page 18-5 of the GPSA Data Book.
4. Read off P_K at the operating temperature.
5. Check if this is same as assumed value and if not redo procedure.

Method of Winn

1. Estimate convergence pressure and calculate liquid phase analysis.

---

[1] An earlier method proposed by Haddon alone requires the calculation of the liquid phase weight composition and an iterative type of calculation to find critical temperature and pressure of the pseudo heavy component.

2. Calculate weight fraction analysis based on lightest component free basis.
3. Find intersection of operating temperature with binary critical pressure for each heavier component and the lightest component.
4. Multiply pressures obtained by corresponding weight fraction of heavier component. The sum of these values is the calculated P_K
5. Check to see if general assumption was OK Figure 4.4 shows how this is done. Also Example Problem #1 shows this method.

Method of Lenoir and White

1. Assume a convergence pressure and calculate a liquid phase composition (molal volumes satisfactory).
2. Divide the system into a fictitious light component and fictitious heavy component.
3. Calculate the effective BP of the light component (EBP_L) from data on effective EP of compounds given in article and graphs showing correction factors as compared to lightest component. Note: Must estimate effective boiling point of the heavy component while doing this.

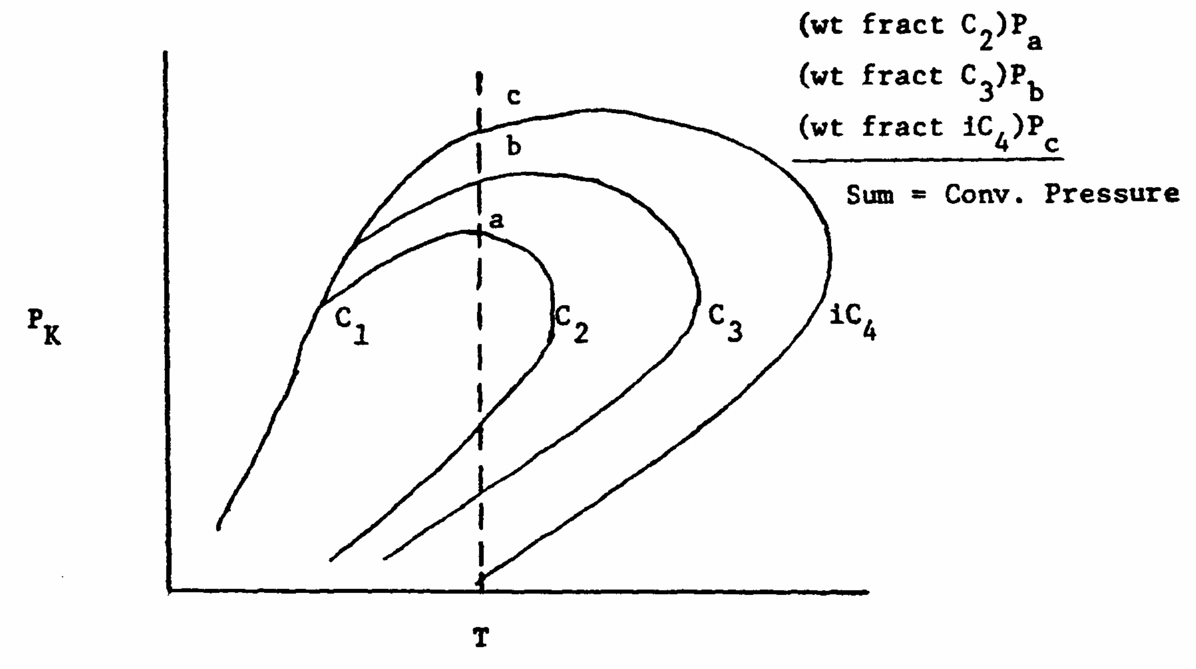

Figure 4.4: Winn Method for Convergence Pressure

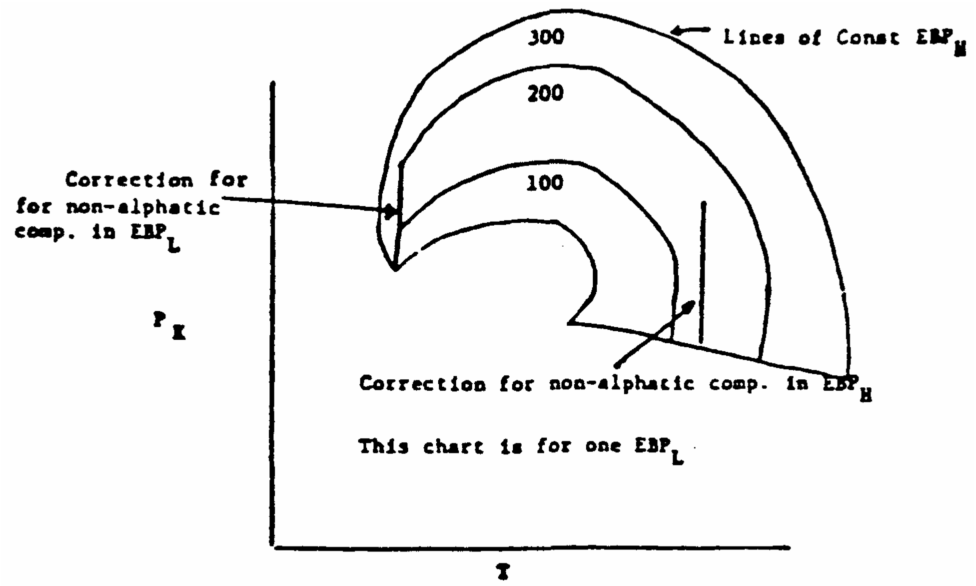

Figure 4.5: Lenoir & White Method for Convergence Pressure

4. Calculate effective BP (EBP_H) of heavy component in similar manner to No. 3.
5. From curves for various EBP_L versus lines of constant EBP_H read off convergence pressure at operating temperature.
6. Recalculate liquid component to see if assumed value is OK

A short cut method assumes that $EBP_L \sim \varepsilon BP$ of lightest 7% EBP_H is εBP of heaviest 40%.

A typical set of curves is shown in Figure 4.5 for an EBP_L of some fixed values.

To correct for non alphatics such as H_2S, CO_2. C_6H_6, etc., a correction factor called the Pressure Function is calculated and depending whether the non alphatic is in the EBP_L or EBP_H function, it is added to the start or finish (or to both ends) of the regular P_K curve. This is shown in Figure 4.5. The presence of these compounds usually give higher convergence pressures.

4.10 Other "K" Data Using the Convergence Pressure Concept

Haddon and Grayson developed a whole series of charts of "K" which are slightly different than the ones given in the GPSA Data Book. These charts are used as a standard by the API. The method requires the calculation of the convergence pressure as previously discussed. The method is reported to be good for heavier mixtures as found in refinery streams, etc.

4.11 “K” Data by Means of Analytic Methods

These methods take into account the specific behavior of each component in the mixture and in one case the relationship of the components to each other. They are particularly suited to computer calculations.

"K" Data by the Chao-Seader Method

This was the first general correlation to try to account specifically for non idealities in the liquid phase. The equation used is

Equation 4-19

$$K_i = \frac{\gamma_i v_i^\circ}{\phi_i}$$

where:

γ_i = activity coefficient of a component in the liquid solution where the fugacity of i in the liquid

Equation 4-20

$$f_i = \gamma_i x_i f_i^{PureL}$$

(f_i^{PureL} is $f\ell_i$ in 11)

v_i° is the fugacity coefficient for the pure liquid component at the system conditions

Equation 4-21

$$v_i^\circ = \frac{f_i^{PureL}}{P}$$

and ϕ_i = fugacity coefficient for a component in the vapour phase

Equation 4-22

$$\phi_i = \frac{f_i}{P_i} = \frac{f_i}{y_i{}^{P}}$$

γ_i is found from the molar volume of "i" and the solubility parameter for the system according to the equation

Equation 4-23

$$\ln \chi_i = \frac{V_i (\delta_i - \delta)^2}{RT}$$

where

V_i = liquid molar volume of "i"

δ_i = solubility parameter for "i"

δ = solubility paramter for the system

The solubility parameter is defined by

Equation 4-24

$$\delta = \frac{\Delta E^{0.5}}{V_i}$$

Where:

ΔE is the change in internal energy going from a liquid to a vapour. All the above can be found from properties of pure components.

$v_i^{\ 0}$ is found using the Pitzer accentric factor "ω".

Equation 4-25

$$\log \upsilon_i^0 = \log(\upsilon_i)^0 + \omega \log(\upsilon_i)^1$$

where:

$v_i^{\ 0}$ = fugacity coefficient for a simple fluid which can be found in charts of Edmister[14]

$v_i^{\ 1}$ = fugacity coefficient correction factor from Edmister[14]

ω = accentric factor as discussed in Chapter 2 and listed for each compound in the GPSA Data Book in Section 16. This is the same as in the method of finding the enthalpy given in Chapter 2.

Or

v_i^0 and $v_i^{\ 0}$ can be found from the two following equations.

Equation 4-26

$$\log(\upsilon_i)^0 = A_0 + \frac{A_1}{T_R} + A_2T_R + A_3T_R^2 + A_4T_R^3 + \left(A_5 + A_6T_R + A_7T_R^2\right)P_R + \left(A_8 + A_9T_R\right)P_R^2 - \log P_R$$

Equation 4-27

$$\log(\upsilon_i)^1 = A + BT_R + \frac{C}{T_R} + DT_R^{\ 3} - 0.25(P_R - 0.6)$$

where:

A, A_2, etc. are constants as are B, C, D, etc.

ϕ_i is found by use of the Redlich Kwong equation also given in Chapter 2. It is

Equation 4-28

$$P = \frac{RT}{v-b} - \frac{a}{T^{0.5}\,V(V+b)}$$

or in terms of the compressibility factor z

Equation 4-29

$$z = \frac{1}{1-h} - \frac{A^2}{B}\left(\frac{h}{1+h}\right)$$

Equation 4-30

$$h = \frac{BP}{z}$$

where:

> A and B are constant for component expressed in terms of their critical conditions and are for the mixture A_i and B_i are for the pure component and Z is the mixture.

Then ϕ_i can be found from

Equation 4-31

$$\ln\phi_i = (Z-1)\frac{B_i}{B} - \ln(A-BP) - \frac{A^2}{B}\left(\frac{2A_i}{A} - \frac{B_i}{B}\right)\ln\left(1+\frac{BP}{Z}\right)$$

The limitations of the Chao-Seader Equation have been well discussed by Lenoir He suggests the equation is good for pressures up to 2000 psi (14,000 kpa) and temperatures of 100°F to 500°F (-75°C to 260°C). Also the liquid should not contain more than 30% methane by mole fraction.

The Grayson Streed[16] modification which is a very similar method to the Chao-Seader has been used very successfully at temperatures of -200°F to 900°F (-130°C to 480°C) and to 3000 psia (21,000 KPA)

There is also a modification by Wilson of the Redlich Kwong Equation that is available through the GPSA as the mark V computer program[9].

"K" Data by the Soave Redlich Kwong Equation[18]

As discussed in chapter 2, Soave developed a modification of the Redlich Kwong Equation

Equation 4-32

$$P = \frac{RT}{V-b} - \frac{aT}{v(v+b)}$$

Suitable rules for mixes using interaction coefficients are proposed.

The Soave Equation "K" is available from the GPSA as a computer program.

This program is considered to give good data over a wide range of temperatures and pressures.

"K" Data by the Peng Robinson Equation

As discussed in Chapter 2, these authors also modified the Redlich Kwong Equation

Equation 4-33

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}$$

This equation can be used to find "K" accurately over a wide range of temperatures and pressures. It is available as a computer program through the GPSA.

"K" Data by the Benedict-Webb-Rubin Equation (Starling Modification)

The BWRS equation (Starling's modification of the BWR equation of state) has the same basic form as the BWR equation, but contains two additional adjustable parameters. The BWRS equation has the following form (see also equation 2.5, with mixing rules given in Table 2.2)

Equation 4-34:

$$P = RT\rho + \left(B_0RT - A - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4} \right)\rho^2 + \left(bRT - a - \frac{d}{T} \right)\rho^3 + \left(a + \frac{d}{T} \right)\alpha\rho^6 + \frac{c\rho^3}{T^2}\left(1 + \chi\rho^2\right)\exp\left(-\chi\rho^2\right)$$

Where:

p is the absolute pressure

T the absolute temperature

ρ the molar density

R the universal gas constant.

Mixing rules used to obtain mixture parameters for the BWRS equation are as given in Table 4.1.

Table 4.1: Mixing Rules - BWRS Equation

$$B_0 = \sum_i x_i\, B_{0i}$$

$$b^{1/3} = \sum_i x_i b_i^{1/3}$$

$$A_0 = \sum_i \sum_j \left(\frac{m_{ij}}{2} \right)^3 x_i x_j A_{0i}^{1/3} A_{0j}^{1/2}$$

$$a^{1/3} = \sum_i x_i a_i^{1/3}$$

$$C_0 = \sum_i \sum_j \left(\frac{m_{1j}}{2} \right)^3 x_i x_j C_{0i}^{1/2} C_{0j}^{1/2}$$

$$\alpha^{1/3} = \sum_i x_i \alpha_i^{1/3}$$

$$\chi^{1/2} = \sum_i x_i \chi_i^{1/2}$$

$$c^{1/3} = \sum_i x_i c_i^{1/3}$$

$$D_0 = \sum_i \sum_j \left(\frac{m_{ij}}{2} \right)^4 x_i x_j D_{0i}^{1/2} D_{0j}^{1/2}$$

$$d^{1/3} = \sum_i x_i d_i^{1/3}$$

$$E_0 = \sum_i \sum_j \left(\frac{m_{ij}}{2} \right)^5 x_i x_j \, E_{0i}^{\frac{1}{2}} \, E_{0j}^{\frac{1}{2}}$$

where x_i is the mole fraction of the "ith" component for the homogeneous phase under consideration, and parameters with subscript "i" refer to the "ith" pure component. The BWRS mixing rules contain a binary interaction parameter (m_{ij}) for each pair of components. The interaction parameters have little effect on bulk properties such as density and enthalpy but can greatly improve K-value predictions.

The BWRS equation is a very good overall thermodynamic prediction method available in the gas processing industry. It is applicable to all types of gas processes including cryogenic expander and absorption of oil plants. It may not be accurate for heavy gas reservoir systems such. as gas condensates or volatile oils or for natural gas—heavy crude systems at processing conditions.

The procedure for calculating "K" is as follows:

1. Perform a flash calculation on the mixture using arbitrary "K".
2. From the vapour and liquid composition calculate the vapour and liquid density.
3. Using the BWRS equation above for fugacity calculate the individual fugacities for each component.
4. Now the fugacities of individual components in the vapour phase and liquid must be equal, i.e.

Equation 4-35

$$f_i^v = f_i^\ell$$

Therefore steps 1, 2, 3 are replaced until this condition is satisfied. This method of course requires computer programs for its use but is generally quite good.

"K" Data by the Prausnitz-Chueh Correlation

This method uses the same basic equation as the Chao—Seader but uses different methods for finding the fugacity, activity, etc. Prausnitz has allowed for the effect on the presence of other components on the constants for individual components in calculating the fugacities, molar volumes, etc. For example, in the calculation of ϕ_i of Equation (18) the Redlich Kwong equation is still used by a binary interaction coefficient is added, i.e. the same as used in the BWRS mixing rules as previously discussed. This data is found from experimental data on binary systems. For example.

Equation 4-36

$$\ln \phi_i = \ln \frac{V}{V-b} + \frac{b_i}{V-b} - \frac{2\sum_i y_i a_{ij}}{RT^{1.5} b} \ln\left(\frac{V+b}{V} \right) + \frac{ab_i}{RT^{1.5} b^2} \left[\ln \frac{V+b}{V} - \frac{b}{V+b} \right] - \ln z$$

This equation corresponds to Equation (31) but the interaction coefficient a_{ij} is added and "a" and "b" are evaluated differently and have different mixing rules. The small "a" and "b" are the constants in the Redlich equation.

The other important change is that the requirement of sometimes having a hypothetic liquid state for the development of the term v_i^0 is avoided by the development of an assymetrical standard state. For the details of the method please refer to reference 12 or suggested reading reference 2.

4.12 A Comparison of the Methods of Determining "K"

The accuracy of the various equations has been checked under special conditions, i.e. low temperatures and high pressure. Some comparative data versus experimental values are given in Tables 4.2 and 4.3. The selection of the appropriate equation of state or method for "K" values is given in references 4 and 5 of the reading list.

Table 4.2: Comparison of Experimental Methane K-Values at -75°F Taken from the C_1 – C_3 Binary Data

P psia	Experimental	1972 Charts P_K = 1000	1966 Charts P_K = 1000	Soave	Prausnitz - Chueh	P-V-T Mark V	Choa-Seader	K-Value
100	10.3	10.2	10.8	10.10	10.57	10.2	7.65	10.65
150	7.00	6.9	6.7	6.73	7.03	6.80	5.24	7.36
300	3.58	3.56	3.25	3.44	3.48	3.46	2.85	3.63
400	2.66	2.65	2.45	2.61	2.60	2.615	2.27	2.63
500	2.13	2.12	1.94	2.11	2.08	2.10	1.925	2.07
600	1.76	1.80	1.67	1.77	1.74	1.76	1.806	1.72
700	1.49	1.56	1.45	1.51	1.51	1.50	1.56	1.49
800	1.28	1.36	1.28	1.33	1.35	1.30	1.46	1.32
900	1.122	1.18	1.14	1.167		1.134	1.39	1.12

P_c = 944

Table 4.3: Comparison of Natural Gas Condensate K-Values with those Predicated by Several Correlations for -100°F and 400 psia

Comp.	Experimental	1972 Charts P_K = 900 psia	1966 Charts P_K = 900 psia	Soave	P-V-T Mark V	Choa-Seader	K-Value
N_2	12.164	8.1	8.1	11.686	13.561	12.049	12.267
CO_2	.554	.559		.548	.516	.364	.801
C_1	2.316	2.24	1.90	2.129	2.338	1.938	2.273
C_2	.159	.160	.167	.147	.144	.144	.1605
C_3	.0221	.0261	.0267	.0211	.0206	.0233	.0256
iC_4	.0068	.0085	.0085	.0054	.0052	.0075	.0073
nC_4	.0044	.0055	.0055	.0031	.0029	.0045	.0045
iC_5	.0014			.0008	.0008	.0018	.0016
nC_5	.0009			.0005	.0005	.0011	.0010

Table 4.4: Recommended Ranges of Application of K-Value Predication Methods

Item	Chao-Seader	Grayson Stread	Lee-Erbar[20]	SBWR	Soave RK	K-Val[21]	Peng Robinson	Mark V

Temp lower limit	-100^{0}F	-200^{0}F	-260^{0}F	-260^{0}F	-260^{0}F	-300^{0}F	-260^{0}F	-240^{0}F
Temp upper limit	+500^{0}F	+900^{0}F	+300^{0}F	+300^{0}F	+600^{0}F	+300^{0}F	+800^{0}F	+200^{0}F
Pressure, upper limit	1500-2000 psia	2500 psia	1500 psia	3000 psia	5000 psia	Atmos to 1800	5000 psia	1500 psia
Pressure:Value of Conv. Point	80%	80%	85%	90-95%	90-95%	Not stated	Up to critical point	Not stated
Component limits	-	-	Paraffin hydrocarbons only, no C_7+, H_2S, CO_2, N_2	C_7+ predictions erratic	No H_2	-	No data for H_2 or He	Not accurate with high CO_2
Comments	Excellent Ks below 0^{0}F provided pressure below conv.pressure; methane and ethane K's sensitive to C_7+. Liquid not to contain >30% CH_4	Best for H_2 containing systems, can be used for hydrocarbons above C-S limits. Methane, ethane K's sensitive to C_7+	Excellent low temperature K except close to critical point	Excellent low temperature K, problems with 10 component mixtures	Probably the best correlation for K	Not accurate when CH_4 is >30% in liquid		

4.13 Calculations Involving K Factors

Dewpoint

This is when the first drop of liquid begins to form.

Equation 4-37

$$\sum_{i=1}^{n} y_i = 1.0$$

and

Equation 4-38

$$\sum_{i=1}^{n} x_i = 1.0$$

Equation 4-39

$$x_i = \frac{y_i}{K_i}$$

Now since we know "y" we calculate the temperature or pressure (the one not given) at which x's add up to 1 or 100%.

Bubble Point Calculation

The reverse of a dewpoint calculation is a bubble point calculation. In this case we wish to determine when the first bubble or gas starts to form. Now here we know x, the liquid component. We add up all the y's from the equation:

Equation 4-40

$$y_i = K_i x_i$$

so that the sum of y = 1 or 100%. i.e.

Equation 4-41

$$\sum_{i=1}^{n} y_i = 1.0$$

Make a table x, K, Y = Kx. Find the proper temp. or press. when:

Equation 4-42

$$Kx = 1.0$$

Note: All these calculations are best done using some sort of computer program if it is available. These illustrations are given for example only.

Example Problem 4.1

Find the dewpoint of the gas given in the table below. The gas is the overhead from an absorber.

The operating pressure is 1000 psia. Set up a table as shown below. Initially assume P_K = 2000 psia

Comp.	**Mole %**	$K_{1000}^{0°F}$ *	$\frac{Y}{K}$	$Try\,K_{1000}^{-20}$	$\frac{Y}{K}$	$Try\,K_{1000}^{-30}$	$\frac{Y}{K}$
N_2	0.30	7.4	0.04	6.2	0.05	5.5	0.06
C_1	91.63	2.0	45.90	1.8	50.80	1.7	54.00
C_2	5.72	0.5	11.52	0.42	13.62	0.39	14.70
C_3	1.63	0.16	10.20	0.13	12.50	0.12	13.60
iC_4	0.29	0.084	3.47	0.07	4.16	0.06	4.81
nC_4	0.31	0.060	5.17	0.048	6.45	0.04	7.75
iC_5+	0.12	0.030	4.00	0.022	5.45	0.016	7.50
Total	**100.00**		**80.30**		**93.03**		**102.42**

* 1957 K data see examples further on in book on effect of different "K" data.

By interpolation the dewpoint is -27°F.

Now check assumption of P_K ; if using curve on P. 172 NGSMA Book

(1957) = 1800 psi; if using curve on P. 222 NGPSA (1966) = 1900 psi.

If using the GPSA (1972) data book = 1800 psi.

Example Problem 4.2

At depropanizing tower is operating with all the overhead product condensing. Determine the tower operating pressure. Assume this pressure is 10 psi greater than the accumulator pressure. The condensing temperature is 80°F.

The overhead product has an analysis of the following:

	Mole %
C_2	3.0
C_3	95.0
iC_4	2.0

Assume a P_K of 800 psi.

Solution

Find the accumulator pressure by doing a bubble point.

Comp.	Mole %	K^{80}_{150}	KX	K^{80}_{160}	KX
C_2	3.0	2.9	8.7	2.7	8.1
C_3	95.0	0.98	93.0	0.96	9.1
iC_4	2.0	0.44	0.9	0.42	0.8
Total			**102.6**		**100.0**

Bubble point pressure is 160 psia.

Tower pressure is 170 psia or 155.3 psig.

A comparison of a dew point calculation using different K data is shown below.

Table 4.5: A Comparison of a Dew Point Calculation Using Different K Data

Comp.	Mole %	NGSMA K^{0}_{1000}	$\frac{Y}{K}$	NGPSA K^{0}_{1000}	$\frac{Y}{K}$	NGPSA K^{0}_{1000}	$\frac{Y}{K}$
N_2	0.30	7.40	0.04	3.9	0.75	3.9	0.75
C_1	91.63	2.0	45.90	1.95	47.10	2.1	43.50
C_2	5.72	0.5	11.52	0.40	14.30	0.46	12.50
C_3	1.63	0.16	10.20	0.135	12.20	0.17	9.60
iC_4	0.29	0.084	3.47	0.088	3.30	0.084	3.47
nC_4	0.31	0.060	5.17	0.046	6.72	0.060	5.17
iC_5	0.12	0.030	4.00	0.021	5.71	0.030	4.00
Total	**100.00**		**80.30**		**89.98**		**78.99**

Vapour Liquid Calculations

Another important calculation is determining the amount of liquid and vapour present in a mixture when the pressure and temperature are known. This can happen for inlet separators, low pressure separators, condensate feed tank, overhead accumulators, etc.

where:

F = feed as 1.00 or 100 moles

V = overhead moles in units of feed
L = bottoms moles in units of feed
z = mole % or mole fraction of feed
y = mole % or mole fraction component in overhead
x = mole % or mole fraction component in bottom

Equation 4-43

$$F = V + L$$

or for component i

Equation 4-44

$$z_i F = y_i V + x_i L$$

Now

Equation 4-45

$$y_i = K_i x_i$$

Equation 4-46

$$zF = KxV + xL$$

Equation 4-47

$$zF = x(VK + L)$$

Divide both sides by L and transpose

Equation 4-48

$$x = \frac{\frac{zF}{L}}{K\frac{V}{L} + 1}$$

Now

Equation 4-49

$$\sum_{i}^{n} x = 1.0$$

The method actually is as follows:

1. Select "K" for each component at the temperature and pressure of the system.
2. Assume an L and thus a V.
3. Calculate L from

Equation 4-50

$$\sum_{i=1}^{n} x = \sum_{i=1}^{n} \frac{zF}{K\frac{V}{L}+1} = L$$

4. Check this value against assumed value.
5. Repeat calculation until assumed value is equal to calculated value.

Example Problem 4.3

Rich oil from an absorber is sent to a rich oil flash drum which operates at 100°F and 300 psig. It is desired to determine the composition and quantity of gas that comes from the rich oil flash drum. The amount of rich oil is 65,931 moles per day and the composition is given in the following table.

			Assume L = 90.0 moles		Assume L = 88.97 moles				
Comp.	**Feed Mole %**	⊕ K_{315}^{100}	$\left(K\frac{V}{L}+1\right)$	$\left(\frac{z}{K\frac{V}{L}+1}\right)$	$K\frac{V}{L}+1$	$\frac{z}{K\frac{V}{L}+1}$	**Moles of Liquid**	**Moles of Vapour**	**Mole % Vapour**
N_2	00.12	48.18	6.3	0.02	6.85	0.02	0.02	0.10	0.93
C_1	16.63	10.01	2.10	7.93	2.21	7.42	7.42	9.21	83.53
C_2	4.99	1.92	1.21	4.11	1.230	4.03	4.03	0.96	8.71
C_3	6.01	0.66	1.07	5.63	1.080	5.56	5.56	0.45	4.10
iC_4	2.04	0.31	1.034	1.97	1.038	1.96	1.96	0.08	0.68
nC_4	4.37	0.22	1.025	4.26	1.027	4.25	4.25	0.12	1.08
iC_5	1.75	0.11	1.012	1.73	1.012	1.73	1.73	0.02	0.21
nC_5	1.29	0.084	1.009	1.21	1.009	1.28	1.28	0.01	0.12
C_6	3.74	0.031	1.004	3.73	1.004	3.73	3.73	0.01	0.13
[1] C_{10}	59.06	0.007	1.001	59.00	1.001	59.00	59.00	0.06	0.51
Total				**88.61**		**88.98**	**88.98**	**11.02**	**100.00**

Note: Assume P_K = 5000 (Convergence pressures are quite high with absorber oils).

$$\text{Amount of vapour per day} = \frac{11.02}{100.00}(65{,}931)(378.9) = 2.75\ MMSCFD$$

4.14 "K" Data for Special Compounds or Systems

These are discussed in some detail in the GPSA Data Book and in the literature. For example methyl mercaptan data is given in the literature (see Haddon and Grayson article). It is supposed to have a “K” value of about 10% greater than isobutane. Also, hydrocarbon systems with hydrogen

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⊕ Computer Values from NGSMA (1957)

[1] Assume to be decane (C_{10}). Could also possibly use data from "K" versus Boiling Point Curves. Assume C_{10} to be Lean Oil

and nitrogen have been discussed in some detail by Lenoir. The presence of H_2 particularly modifies the “K” value for methane and other gases considerably.

For determining the "K's" for sour gas the method of Lenoir and White or the Soave method is probably as good as any when using charts.

The Peng Robinson or the Soave methods give reasonable values for sour gas "K's" from the computer programs.

To find the "K" value for heavy components we can either use data in the NGPSA book for various boiling point materials or by plotting of log "K" versus $\frac{1}{T_b}$ for various components in the mixture at the system pressure and extropolate to the T_b of the heavy component. Other methods are given in Campbell.

Also please read Section 25 of the English GPA data book for general discussion on Equilibrium Ratios.

Example Problem 4.4

An existing tower that has a design operating pressure of 100 psia is available for use in debutanizing a hydrocarbon feed of the following composition:

	Mole %
C_2	0.8
C_3	35.4
iC_4	10.6
nC_4	21.7
iC_5	5.0
nC_5	11.6
C_6	10.3
C_7+	4.6

The fractionation is such thet the top product is not to contain more than 2.0% of iC_5 and the bottom is not to contain more than 3.0% of nC_4.

Determine the type of cooling medium that has to be used with this tower.

a) Air cooling-product condensing temperature 120°F.

b) Cooling Tower water; product condensing temperature 95°F.

c) Once through river water product condensing temperature 70°F.

d) Propane refrigeration product condensing temperature 40°F

Example Problem 4.5

A Heat exchanger in a LNG plant which is chilling natural gas from +60°F to -20°F has as the chilling medium a mixed refrigerant of the composition listed in the table below. The refrigerant enters the exchanger as a liquid and leaves as a vapour. Determine the ΔT at each end of the exchanger.

	Mole %
N_2	1.0
C_1	83.5

H_2S	6.5
$C0_2$	3.5
C_2	2.8
C_3	1.4
iC_4	0.4
nC_4	0.5
iC_5	0.2
nC_5+	0.2
	100.0

Example Problem 4.6

You are to recommend to your company what "K" correlation to use for an ethane recovery facility that is to process gas of the following composition:

	Mole %
C_1	86.01
C_2	10.35
C_3	2.55
iC_4	0.32
nC_4	0.47
iC_5	0.08
nC_5	0.12
C_6	0.10

This gas is received at 700 psia and 60°F.

The following conditions should be investigated:

1. At the first separator 680 psia and -90°F
2. At the second separator after the expander in which the gas from the first separator is expanded to 300 psia and -135°F

Example Problem 4.7

A gas of the composition given below is cooled to -120°F and 350 psia in an expander plant. It has a high methyl mercaptan (CH_3SH) content. Some concern has been expressed as to whether most of this material will stay in the gas. Please estimate what fraction of the mercaptan will remain in the gas phase after the above referred to chilling has taken place (within 10%). Use the following data:

	Feed Gas Composition Mole %
C_1	93.54
C_2	4.96
C_3	1.25
iC_4	0.10
nC_4	0.15
	100.00

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5.0 Water Hydrocarbon Systems

- Water solubility in natural gas and natural gas liquids.
- Effect of chemical composition on solubility.
- Gas hydrates and their nature.
- The probability of forming gas hydrates, and the preventing of their formation.
- Effect of chemical composition on hydrate formation.

5.1 Why Do We Consider These Systems?

a) Water is present in most reservoirs and raw gas is usually considered to be saturated in the reservoir. This may not be the case, but no detailed work has been done to show that reservoirs are not saturated.

b) The presence of water can cause the formation of what is called hydrates. These are chemical compounds of 2~ and hydrocarbons. If they form in pipelines they cause serious plugging problems.

c) The presence of water in liquid hydrocarbons can cause freezing of liquid lines and stoppage of fuel flow.

d) Water systems can be corrosive, particularly when acid gases are present.

5.2 Typical Water-Hydrocarbon Systems

The systems of water and various hydrocarbons are quite complex. Many liquids, hydrate and solid phases occur. Figure 5.1 shows the temperature composition diagram for propane and water at a fixed pressure of 300 psig (2200 kpa).

To see what happens to a mixture of propane and water, let us consider a 50% C_3 and 50% H_2O mixture at about 350°F (176°C) and then cool it. Initially it is a gas (G). Upon cooling, a liquid phase that is essentially water (L_1) is formed and the gas becomes richer in propane but is still just a gas (G, L_1 are present). On further cooling, a propane rich liquid is formed (L_2) and only two liquid phases are present (L_2 and L_1). Further cooling brings the formation of a propane water hydrate (H) while the propane rich liquid remains. More cooling brings about the formation of solid propane while the hydrate compound remains. The pressure, temperature diagram for C_3 and H_2O is shown in

Figure 5.2. Similar types of diagrams can be developed for other hydrocarbon-water systems. (See Katz, Pages 190 forward).

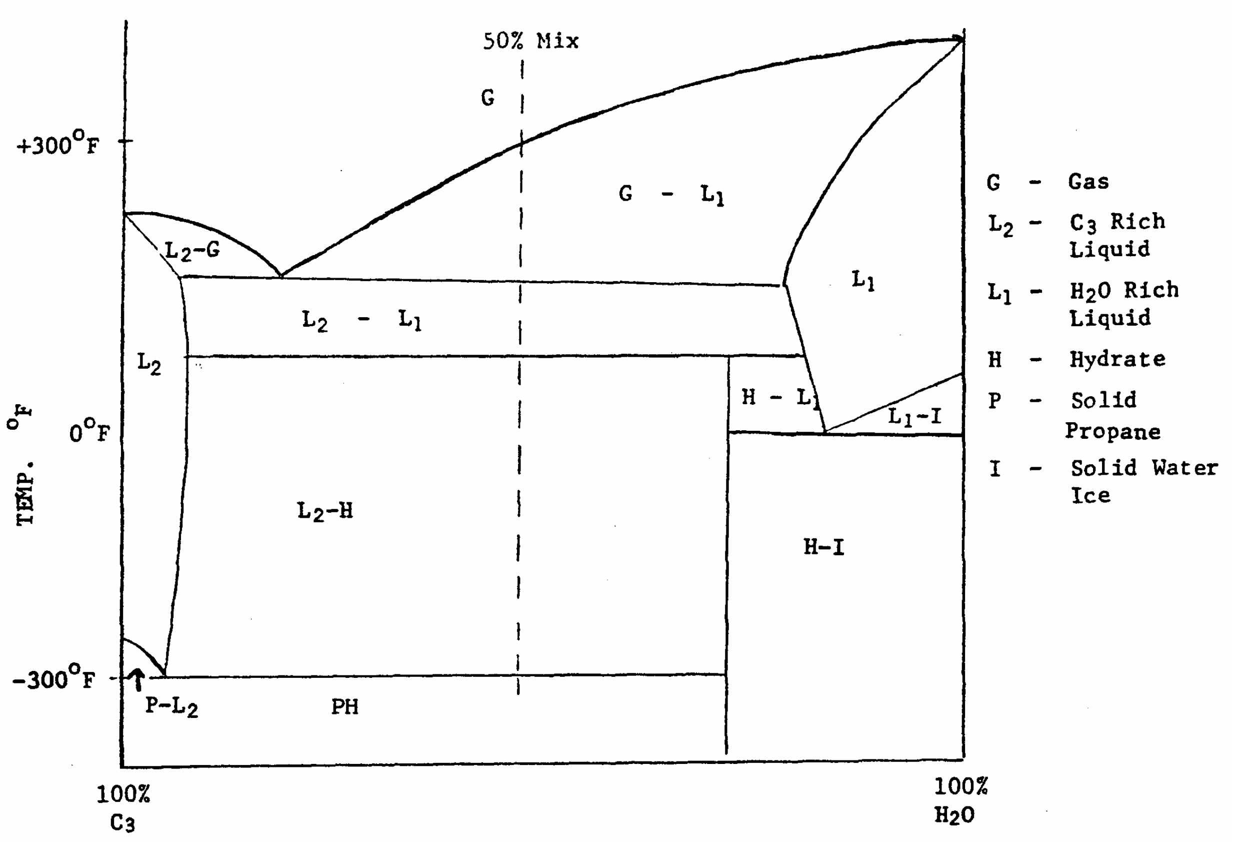


Figure 5.1: Temperature Composition Diagram Propane Water

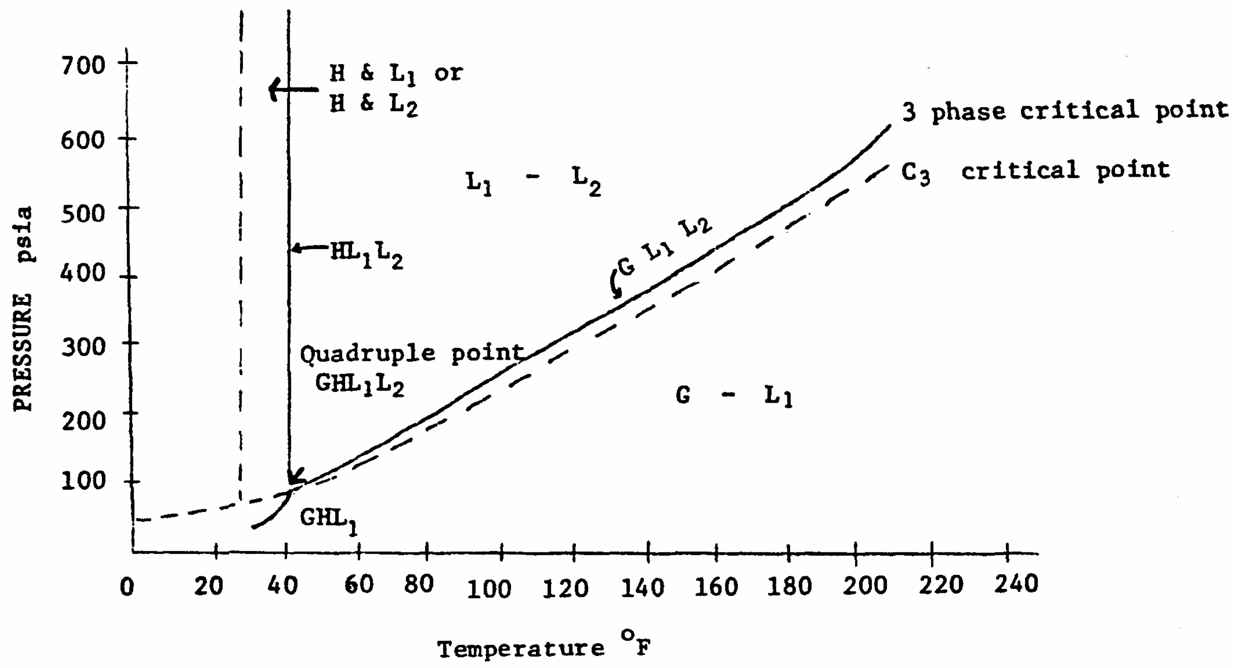


Figure 5.2: Pressure Temperature Diagram Propane Water

5.3 Water Content of Natural Gas

Sweet Gas (Hydrocarbons Only)

Natural gas can contain considerable amounts of water vapour, particularly at high temperatures and low pressures. Figure 5.3, wltich is a reproduction of the chart given in the GSPA SI Data Book shows that as the pressure is increased the water content of natural gas is decreased. This chart also can be used to illustrate why the specification of a water content of 4 lbs per MMSCF for pipeline gas is required in Canada.

The dewpoint of a gas at 800 psia (5500 kpa) with a water content of 4 lbs per MMSCF (65 mg per m^3} is 14°F (-10°C). Since pipeline gas gets down to a temperature of +25°F (-4°C) in the winter even when in a buried pipeline three feet under ground,a water content higher than 4 lbs/MMSCF would result in water condensing in the pipeline which would result in several problems.

Gas Containing Significant Amounts of Non-Hydrocarbons

In the case where there are significant quantities of non-hydrocarbons such as nitrogen, hydrogen sulphide or carbon dioxide present, the water content of the gases are quite different than compared to that obtained from Figure 5.3. Nitrogen does not hold as much water as natural gas. Katz, on pages 197 and 198, discusses this. The acid gases, H_2S, and CO_2 can hold a much greater amount of water, particularly at high pressures. This is explained by the fact that both water and the acid gases are polar compounds and hydrocarbons are not.

Figures 15-21 and 15-22 in the GPSA Data Book give the water content for pure H_2S and CO_2 for calculation purposes.

To find the actual water content of gases containing large amounts of non-hydrocarbons, it is best to consider each non-hydrocarbon component separately, then add the separate fractions of the gas to find the total water content. The equation for this is

Equation 5-1

$$W_{mixture} = Y_{HC} W_{HC} + Y_{H_2S} W_{H_2S} + Y_{CO_2} W_{CO_2}$$

Where:

Y is the mole fraction of each component.

An example of this procedure is given in Example Problem 5.1. This method has worked out quite successfully at Pine Creek, Alberta, where it was found that water content of the sour gas that was to be dehydrated was much higher than that obtained from the sweet gas curves. (For a description of the facilities and some special test work for this field see A. Masuda and P. Krachy).

Method of Wichert

Moore, Heidemann, and Wichert have developed a new method for estimating the water contents of sour natural gas based on extensive field tests of sour gas in Canada. Figure 5.7, 5.8, and 5.9 show this data to sour gas up to 40% acid gas and from 300 to 10,000 psia (2068 to 68,947 kpa).

Note: The figures are given for H_2S as the acid gas component. CO_2 is considered to hold about 75% of what H_2S does, thus if you had a mixture of 20% H_2S 16% CO_2 and the rest hydrocarbons you would use data for 32% H_2S - 68% HC.

Example Problem 5.1

Determine the expected water content of gas of the composition given below. The gas is in the reservoir at 3000 psi and 160°F

	Mole %
N_2	0.4
H_2S	35.0
$C0_2$	10.0
C_1	53.6
C_2	1.0

Method 1

Use the partial water content for each major different component. See Figure 15-21 and Figure 15 - 22 from the GPSA Data Book for the CO_2 and H_2S water content. Then the calculation becomes:

	Mole %	Individual Water Content lbs/MMSCF at 160°F	Partial Water Content	Source of Data
Sweet Gas Comp.	55.0	130	71.5	Fig. 15-14 GPSA Data Book
H_2S	35.0	500	175.0	Fig. 15-22 GPSA Data Book
CO_2	10.0	220	22.0	Fig. 15-21 GPSA Data Book
Total			**268.5**	

Method 2 (Wichert's)

H_2S	35.0
CO_2	10.0 equivalent 7.5 Acid Gas 42.5%
HC	57.5

From Chart 5.8 and by interpolation water content = .78 BBls/MMSCF = 0.223 lbs H_2O/MMSCF

Note: Experimental data on high acid natural gas of a similar composition give a water content data of just over 300 lbs/MMSCF. Thus, either method can be used for calculating water content at high acid gas concentrations.

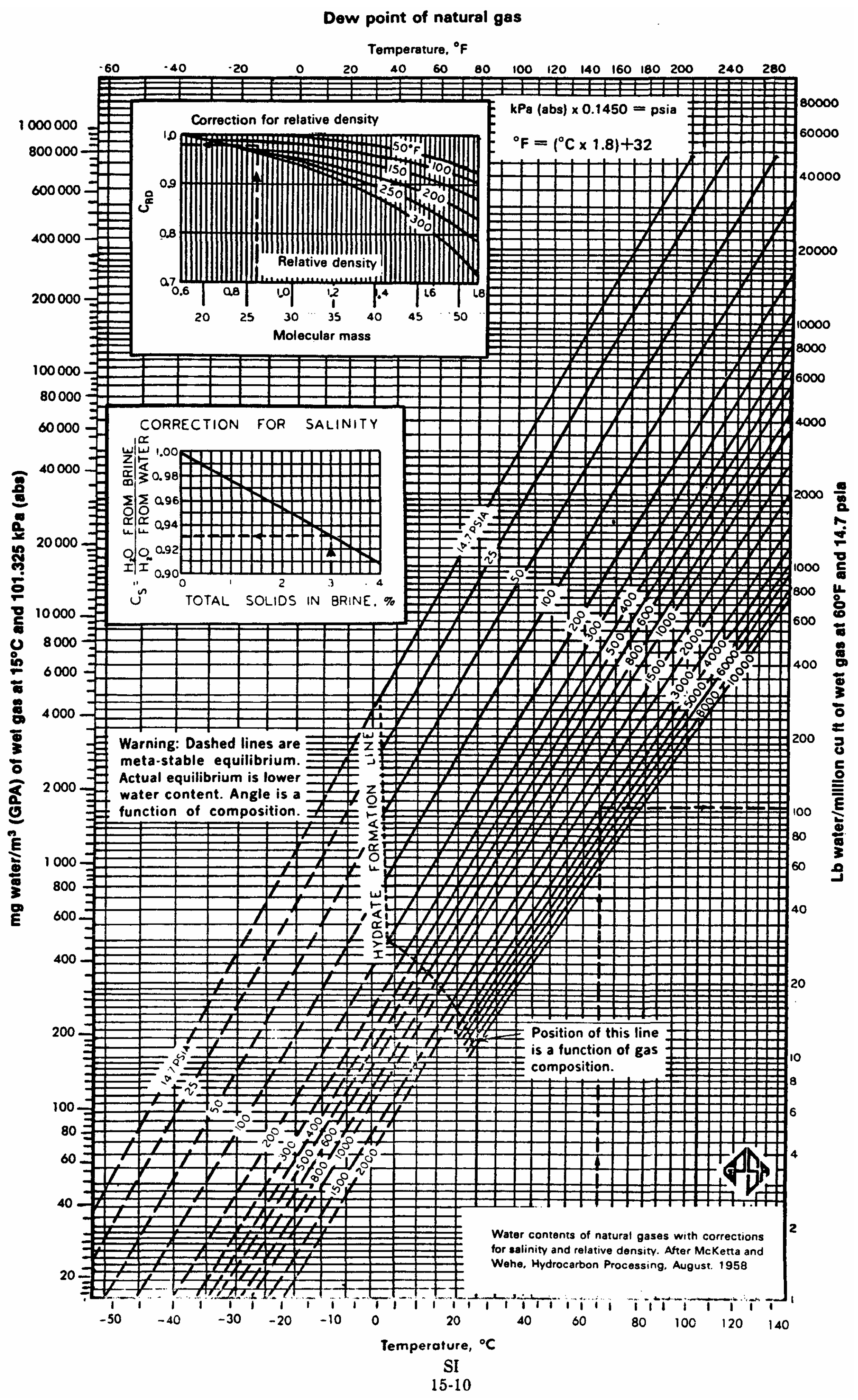


Figure 5.3: Water Contents of Natural Gas with Corrections for Salinity and Relative Density

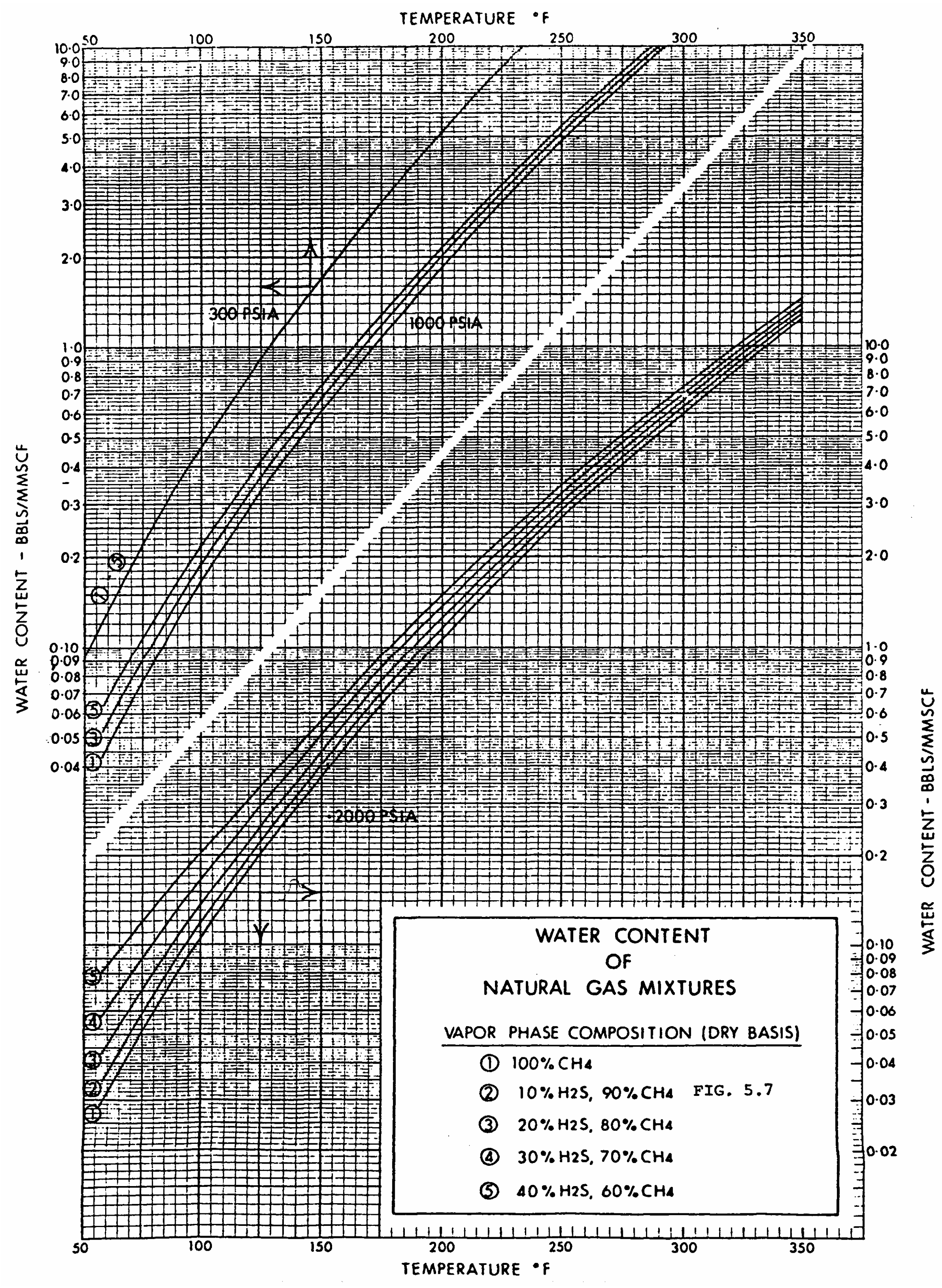


Figure 5.4: Water Contents of Natural Gas Mixtures

5.4 Water Content of Liquid Hydrocarbons

Data for the solubility of water in varying hydrocarbons is presented in GPSA Data Book, P. 15-9, as Fig. 15-13. Hydrocarbons from propane through lube oil are given. Generally hydrocarbons that have been in contact with water must be dried before being stored. A salt tower is often satisfactory for the heavier compounds like diesel oils; this removes the free water. For drying liquid propane from storage wells $CaCl_2$ pellets are often used.

5.5 The Measuring of The Water Content

Water content can be measured by:

a) The use of a Bureau of Mines Dewpoint detector in which the gas is chilled to the point of condensation of the water. Particular care has to be taken when using this apparatus that a water dewpoint and not a hydrocarbon dewpoint is recorded.

b) The use of chemical tests: Karl Fisher Reagent. This is used for trace water determinations.

c) Using chromatography techniques - as described by Lukacs and Robinson.

5.6 Hydrocarbons in Water

The problem of dissolving hydrocarbons by water is primarily that of physical absorption. A Henry's law equation or a modification of it can be used, i.e.

Equation 5-2

$$\overline{Pi} = HXi$$

where:

$\overline{Pi}$ = partial pressure of component i in gas

H = Henry constant for system

Xi = mole fraction of i

or if fugacities are used, $\overline{fi} = HXi$. Henry's law constant for various gases given in Perry and Katz. These values are a function of temperature only.

Data for the solubility of specific compounds or products, such as natural gas, propane, etc., are giveh in Katz on P. 207.

Special data should be collected for the absorption of natural gas by the various sweetening solvents. Figure 5.5 gives the data for monoethanol amine. Diethanol amine absorbs about twice as much and sulphinol considerably more than this. Actual data needs to be published on these systems.

5.7 Hydrates

Gas hydrates are loose chemical compounds of hydrocarbons and water. Some typical formulae are.:

CH_4 - 7 H_2O

C_2H_6 - 8 H_2O

C_3H_8 - 17 H_2O

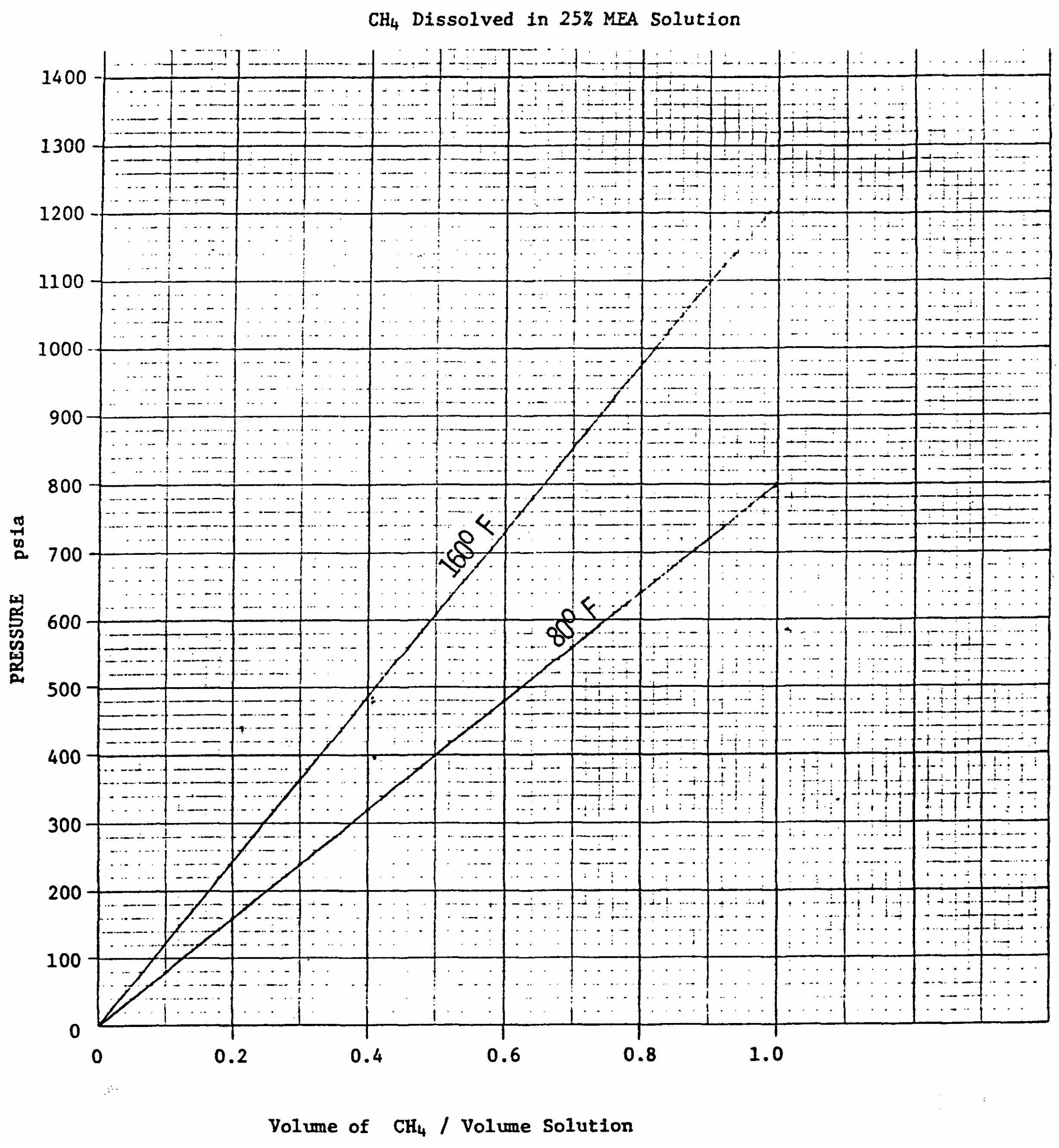


Figure 5.5: CH_4 Dissolved in 25% NEA Solution

Gas hydrates belong to a class of substances called clathrates (see #4 of the Reading List) - A clathrate compound is one formed by the complete enclosure of one or more species of a molecule in a suitable structure formed by another species. When the host structure is water the clathrate is called a hydrate. Gas hydrates have some properties ascribed to chemical compounds and sometimes behave as solutions of gases in crystalline solids. They resemble wet snow in appearance. Two types of structural lattice are generally:

a) Structure I a body centre cubic lattice with 7-8 H_2O in framework. This applies for the smaller molecules like CH_4, C_2 H_6, H_2S

b) Structure II a diamond shape lattice with up to 17 H_20 molecules per gas molecule for heavier molecules.

In both cases, water forms the framework and hydrocarbon fills voids in the centre of the framework or in cavities formed by the water molecules. Note that: The maximum diameter of the cavities is 6-7 Angstroms. A gas having a molecular dimension greater than this diameter cannot form hydrates, thus C_7 and heavier do not hydrate. C_5 will hydrate at 32°F (0°C) and C_6 will hydrate at a lower temperature than this. Gases with a hydrogen from atom in the polar position do not hydrate, i.e. ammonia, alcohols, etc.

Table 5.1 shows the molecular dimension of hydrocarbons.

Table 5.1: Size of Hydrocarbon Molecules

Hydrocarbon	Molecular Dimension °A
C_1	3.882
C_2	4.418
C_3	5.061
iC_4	5.341
nC_4	4.997
iC_5	5.32
nC_5	5.769
nC_6	5.909
C_7	8.88
C_8	7.451
C_9	8.778

Note: Hydrate can form with liquid hydrocarbons present but the right conditions of free water present, proper temperatures and pressures have to occur.

5.8 Conditions for Hydrates to Form

Hydrates form only when free water is present and the system is at a proper temperature and pressure. It should be noted that hydrocarbons from C_1 to nC_4 inclusive only form hydrates. Pentanes and heavier do not above 32°F (0°C) - However, H_2S and CO_2 do. Here are some examples of hydrate conditions:

Table 5.2: Hydrate Formation Conditions

	Min. psia	** Pres. (kpa)	Max. Temp.	** °F (°C)
CH_4	400	(2790)	33	(1)
	600	(4185)	40	(4)
	1000	(6970)	50	(10)
C_2H_6	80	(558)	33	(1)

	400	(2790)	57	(14)

Note: ** Hydrates will form if pressure above these values and temperature below these values.

5.9 Calculation of the Possibility of Hydrates Forming

The possibility of a hydrate forming can be calculated by using the hydration formation graph on Fig. 15-1 of the GPSA Manual. For example, to find the hydrate temperature of a gas with a gravity of 0.62 at 900 psia, one reads off the chart that it is 60°F. Another method of calculating the hydrate temperature is by the use of the hydrate equilibrium constant "$K_{v\text{-}s}$". The equation that is used is:

Equation 5-3

$$K_{v-s} = \frac{y}{x_s}$$

where:

$K_{v\text{-}s}$ = equilibrium constant for vapour solid equilibrium

y = mole fraction of HC on a water free basis

x_s = mole fraction of HC in the solid on a water free basis

Values for $K_{v\text{-}s}$ for C_1, C_2, C_3, iC_4, CO_2 and H_2S are given in the GPSA Data Book, Figure 15-7 to p. 15-12. To find the hydrate condition of a gas at given pressure, a calculation similar to a dewpoint one should be done, i.e.

Equation 5-4

$$\sum \frac{Y}{K} = 1.0$$

Make a table showing given gas composition, then find $\frac{Y}{K}$ for assumed temperature. When $\frac{Y}{K} = 1.0$ then this is the temperature at which hydrate will form. For K value not given in the charts use the following:

1. For n butane take K values for ethane.
2. For N_2 and hydrocarbon compounds heavier than nC_4 take K as infinity. Example Problem No. 2 shows how above calculation is done.

Baillie and Wichert have developed a graphical method for calculating hydrate temperature of sour natural gas. The method is given below and uses Figure 5.11 (metric units) and Figure 5.12 (imperial units).

1. Calculate the relative density (specific gravity) of the gas mixture.
2. Enter the main graph at the pressure on the left side (sloping axis), and move to the right to the H_2S concentration line. Interpolate between lines. Drop down to the gas relative density (gas gravity) line, then follow the slope of the guide line to

the temperature scale at the bottom of the graph. Read the temperature in 0°C (0°F).

3. Obtain the temperature adjustment for the C_3 content from the top left side of the page. Enter this graph along the H_2S scale, move to the right to the C_3 concentration of the mixture and then drop down to the pressure line. Move either right or left to obtain the C_3 content adjustment in 0°C (0°F). The values on the left side are negative.
4. Add the C_3 adjustment~obtained in Step 3 to the value obtained in Step 2. The result is the estimate of the hydrate temperature at the given pressure for the gas mixture.

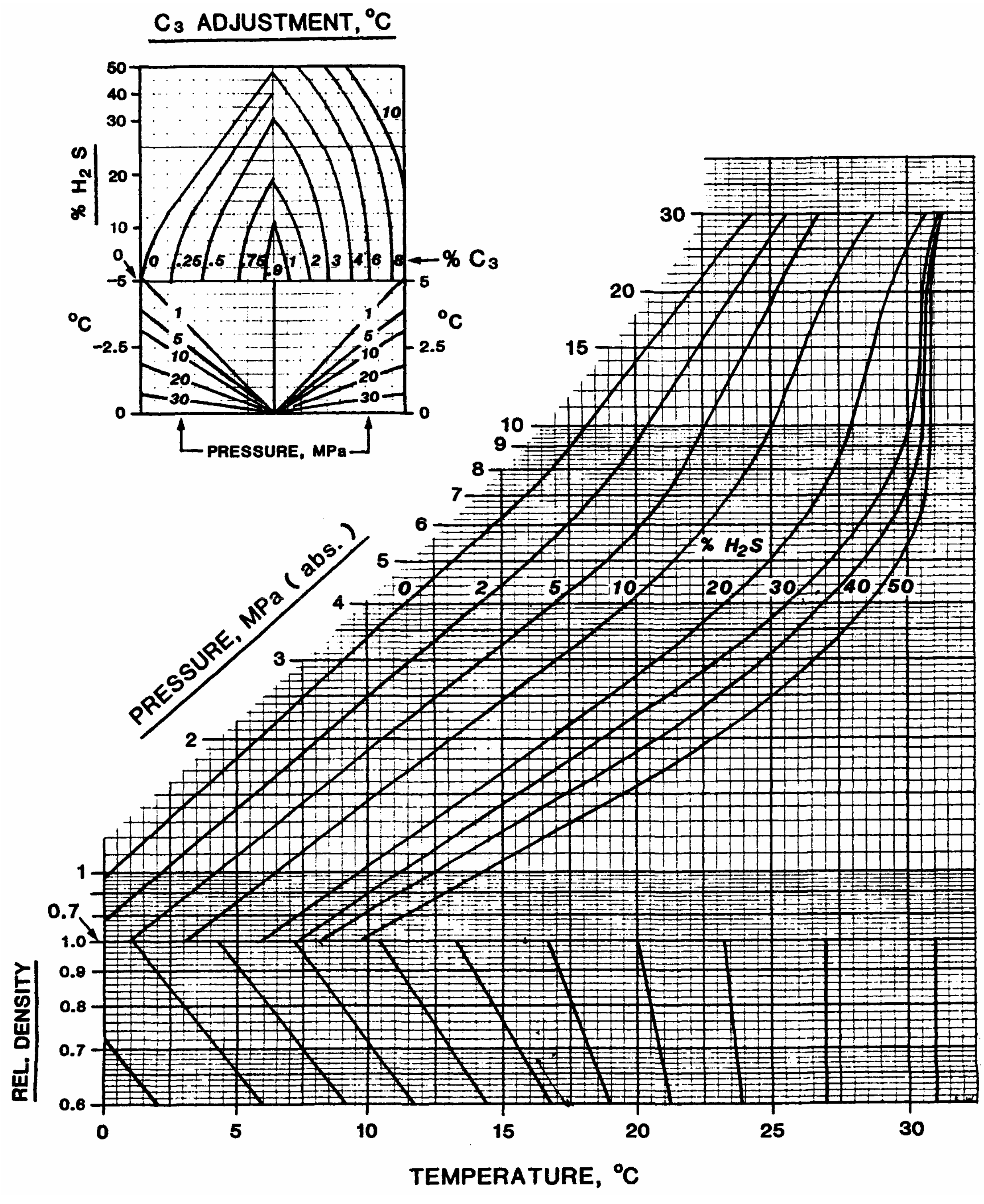


Figure 5.6: Hydrate Chart for Sour Natural Gas (SI Units)

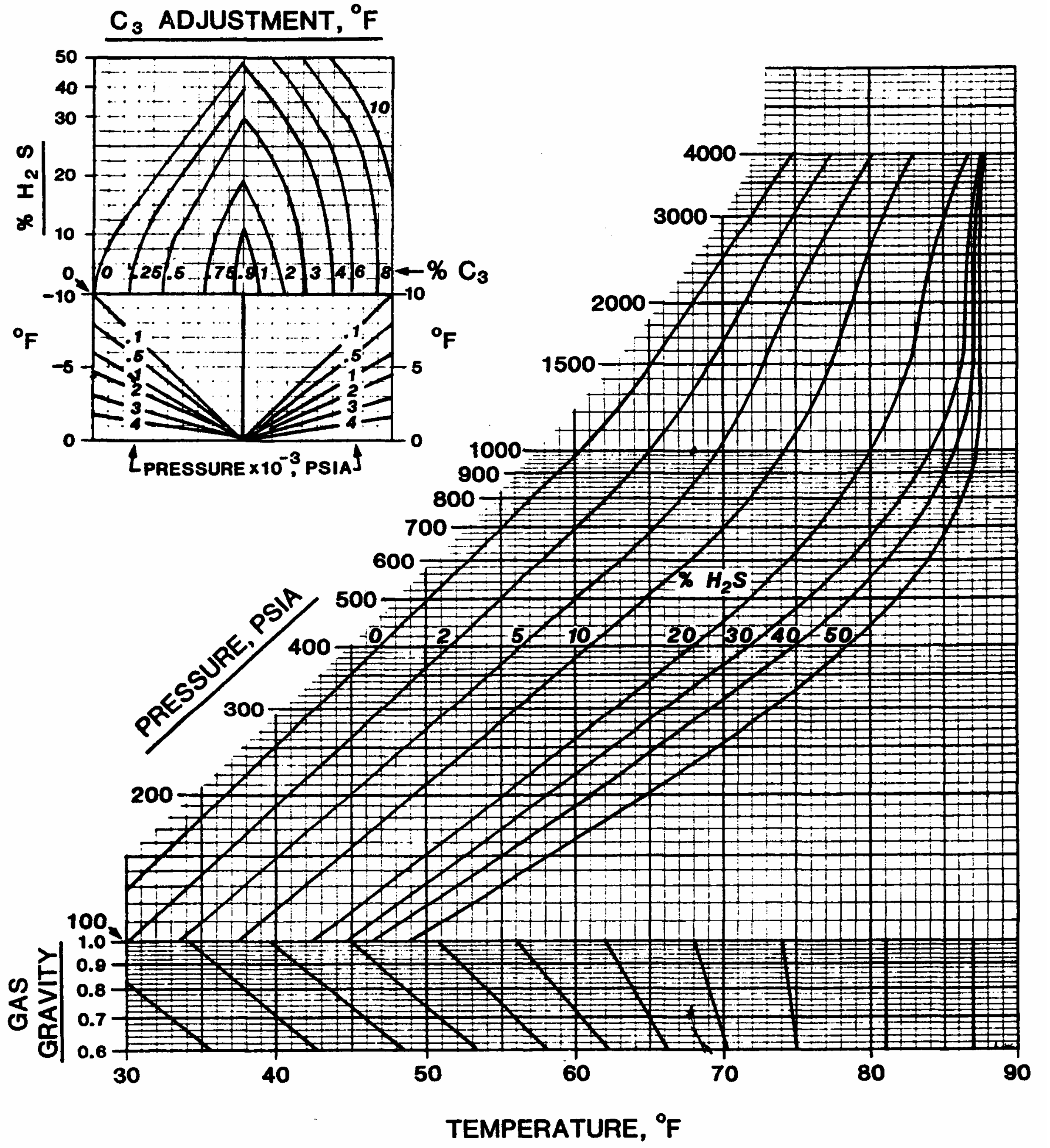


Figure 5.7: Hydrate Chart for Sour Natural Gas (Imperial Units)

Example Problem 5.2

Determine the hydrate point of the gas of the composition given in the table below when the gas is at 1200 psig.

Comp.	**Mole %**	**Kvs at 65°F**	$\frac{Y}{K}$	**Kvs at 70°F**	$\frac{Y}{K}$
N_2	4.2	∞	0.0	∞	0.0
H_2S	6.4	0.25	25.6	0.37	17.3
CO_2	4.4	10.0	0.4	25.0	0.2
C_1	78.0	1.18	66.1	1.21	64.4
C_2	3.2	0.85	3.8	1.15	2.8
C_3	1.2	0.10	12.0	0.16	7.5
* nC_4	0.5	0.85	0.6	1.15	0.4
iC_5	0.3	∞	0.0	∞	0.0
nC_5	0.5	∞	0.0	∞	0.0
C_6	1.3	∞	0.0	∞	0.0
Total			**107.5**		**92.6**

* Use K_{vs} value for ethane for n Butane.

By interpolation the hydrate point is 69°F. If gravity of gas is calculated from composition it is equal to $\frac{20.7}{28.9} = 0.71$. Check hydrate temperature using this value. From 15-1, P. 15-2, hydrate temperature is 67°F. This is a good check (The value by the Wichert chart is 71.).

Also given in Fig. 15-2 to 15-6 of the GPSA Data Book are graphs showing the permissible expansion of natural gases without hydrate formation. This is quite important, as often when a well is choked at the wellhead, this condition can occur.

5.10 The Prevention of Hydrates

Hydrates form under the following conditions:

a) At proper conditions of temperature and pressure.
b) When free water is present.

Also, generally they form in areas of great turbulence.

To prevent hydrates from forming, the following methods can be used:

1. Keep the gas above the hydrate temperature.
2. Remove the water from the gas so that free water will not condense out.
3. Add chemicals to the gas to combine with the water. The chemicals mostly used are methanol, glycols and sometimes ammonia. Glycols are generally used for continuous processes while methanol is used for emergencies.

A well known equation, called the Hanunerschmidt equation, is used to determine the concentration of chemical in the final solution.

Equation 5-5

$$d = \frac{KW}{100M - MW}$$

where:

d = number of °F gas hydrate freezing point is lowered.

W = wt % of final glycol concentration.

M = mole wt. of compound used for hydrate suppression.

K = a constant = 2335 for methanol, ethanol, ammonia; = 4000 for glycols

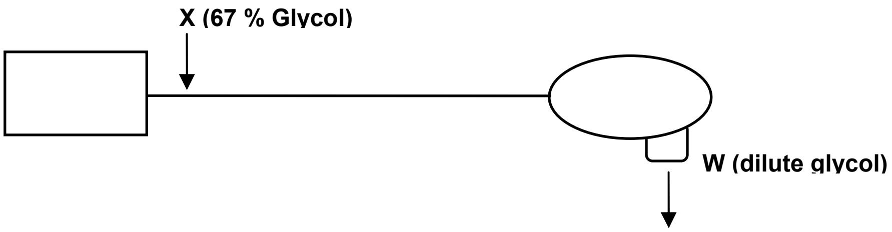
In metric units i.e. d in °C then k = 1297 for methanol, and 2222 for glycols. Thus we can calculate the concentration of final glycol solution and if we know what the initial concentration is (for hydrate inhibition solution strengths used are about 75% to 80%) then the amount to circulate can be calculated.

Example Problem 5.3

Determine the amount of 67% by weight mono ethylene glycol to be circulated in a gas gathering unit that has a central glycol concentration unit.

Gas Pressure	1000 psig
Gas Temperature from well	85°F
Ground Temperature	40°F
Gas Specific Gravity	0.75
Total gas handled per day	8 MMSCF

From the hydrate formation curve, it is determined that a saturated gas with a specific gravity of 0.75 at 1000 psig has a hydrate point of 67F. Thus, the hydrate depression required is 67 - 40 or 27F. Assuming mono ethylene glycol (mol. wt. 62.1) is utilized, the following substitutions are made in the Hammerschmidt equation and W determined:



$$d = \frac{4000W}{100M - MW} \qquad 27°F = \frac{4000W}{6210 - 62.1W}$$

W = 29.5 % by wc – EG final concentration.

From Figure 5.3 it is seen that saturated gas at 85°F and 1000 psig contains 39.1 lbs H_2O/MMSCF. When the gas is cooled to 40°F it will contain 9 lbs/MMSCF.

With 8 MMSCF of gas being processed daily, this amounts to

$$\left(\frac{39.1-1}{24\ Hours}\right)(8)=10 lbs/hr$$

that is condensed and has to be handled by the glycol.

Assuming hydrate depression is to be achieved by injecting 67 % by weight ethylene glycol, the injection rate required to produce a final glycol concentration of 29.5 % is calculated.

Do this by a glycol balance.

Let:

X = lb of 0.67 EG/Hr

0.67 X = 0.295 (X + 10)

X = 7.86 lbs/hr required

probably should design pumping capacity for about double this amount.

Example Problem 5.4

Data

Gas pressure 6995 kpa

Gas temperature from Well = 29.4°C

Ground Temperature = 4.4°C

Gas flow = 226,564 m^3/day

Solution

Gas Hydrate temperature = 19.4°C

Ground temperature = 4.4°C

Depression Required = 15°C

Hammerschmidt Equation:

$$15=\frac{2222W}{100(62.1)-62.1W}$$

W = 29.5% by wt. total concentration.

From Figure 5.3:

Water content at 29.4°C = 690 mg/m^3

Water content at 4.4°C = 170 mg/m^3

Difference = 520 mg/m^3

$$mg/hr=\frac{520\,(226{,}564)}{24}=4.91\frac{kg}{hr}$$

Now solve by glycol balance:

0.67X = 0.295 (x + 4.91)

X = 3.86 kg/hr

5.10.1 More Example Problems

Example Problem 5.5

It has been decided to use a molecular sieve unit to dehydrate a gas produced from a reservoir. The reservoir pressure is 3000 psia and at 160°F. The gas has the following composition:

	Mole %
N_2	0.5
H_2S	26.7
$C0_2$	12.3
C_1	57.3
C_2	2.3
C_3	0.8
iC_4+	0.1

The dehydration a 4 hour cycle. on regeneration unit is to be designed to handle 50 MMSCFD of gas on. That is, each bed is on for 4 hours and then 4 hours and cooling.

Determine the length and diameter of the mole sieve vessel. Here is some additional information.

a) The wellhead flowing pressure is 2600 psia and the temperature is 140°F.

b) The design flow for gas through a mole sieve dessicant bed is 30 feet per minute.

c) Allow 2 feet on either side of the molecular sieve bed for an entrance chamber and for a disengaging space.

d) The bulk density of the molecular sieve is 43 lbs/cu. feet.

e) The design absorptive capacity of the sieve is 10% adsorption.

f) The gas is to be dried to a dew point of 10°F prior to entering the pipeline.

g) The unit's design operating pressure is 1440 psig.

Example Problem 5.6

A gas well flows at the rate of 20 MMSCFD directly to a gas plant. It is located 2 moles from the plant. The temperature of the gas leaving the well is 100°F (after the choke) and it is 80°F when it reaches the plant. The gas composition is as follows:

	Mole %
H_2S	27.5
$C0_2$	7.5
C_1	63.0
C_2	1.7
C_3	0.3

Another gas well is found adjacent to the gathering line 1 mile from the plant. It produces only 5.0 MMSCFD and the temperature of the gas leaving the choke is calculated to be 60°F with no heater. Its composition is as follows:

	Mole %
H_2S	5.0

$C0_2$	1.0
C_1	87.0
C_2	5.0
C_3	1.5
iC_4	0.5

The pressure of the gas at each well is 2000 psia. The pipeline pressure at the first well is 1200 psia, at the second well 1100 psia and the plant 1000 psia.

Do you think it is necessary to put a heater at the second well before the choke? If so, how hot would you heat the gas from this well?

Assume temperature drop along the initial gathering line is directly proportional to its length.

Example Problem 5.7

Assume gas field has been discovered just off the Gulf Islands between Vancouver, B.C. and Vancouver Island. The gas composition is as given below. It is anticipated the flowing wellhead pressure will be 2500 psia and it will be choked at the well to 1400 psia and then transported along the bottom of the ocean to a central processing plant on the B.C. mainland at tidewater. The anticipated maximum flow is 200 MMSCFD. It is planned to control the hydrates in the line by injecting an 80% ethylene glycol solution at each welihead. The glycol will be recovered at the plant and re-used. Determine the amount of glycol required for this operation. Express as an 80% glycol solution in lbs/day.

Data:

Ocean minimum temperature	42°F
Reservoir Pressure	3000 psia
Reservoir Temperature	160°F
Wellhead temperature under flowing conditions	110°F
Plant entrance pressure	1200 psia

The gas composition is:

	Mole %
C_1	87.2
C_2	5.6
C_3	3.2
iC_4	1.0
nC_4	2.4
iC_5	0.6

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Search Main Menu

6.0 Flow of Fluids

- Energy relationship
- Gas flow
- Liquid flow
- Two-phase flow
- Measurement of flow and equipment for making fluids flow.

6.1 Introduction

6.1.1 What is a Fluid?

A fluid can be defined as a substance which, when a fixed quantity of the substance is taken, this material assumes the shape of the container that holds it as contrasted to a solid which is a fixed shape (liquid takes half of bottom of container if not enough present). A fluid can be either a gas or a liquid.

6.1.2 Classes of Fluids

There are two major classes of fluids, Newtonian and non-Newtonian. We are concerned in this course, and in the natural gas industry, primarily with Newtonian fluids. However, we should define the two classes. For example, a non-Newtonian fluid is a material like a plastic or tar, etc. and is often characterized by a minimum force required to cause flow, or the shear stress is not directly proportional to the rate of shear stress. Figure 6.1 shows the difference between the two classes.

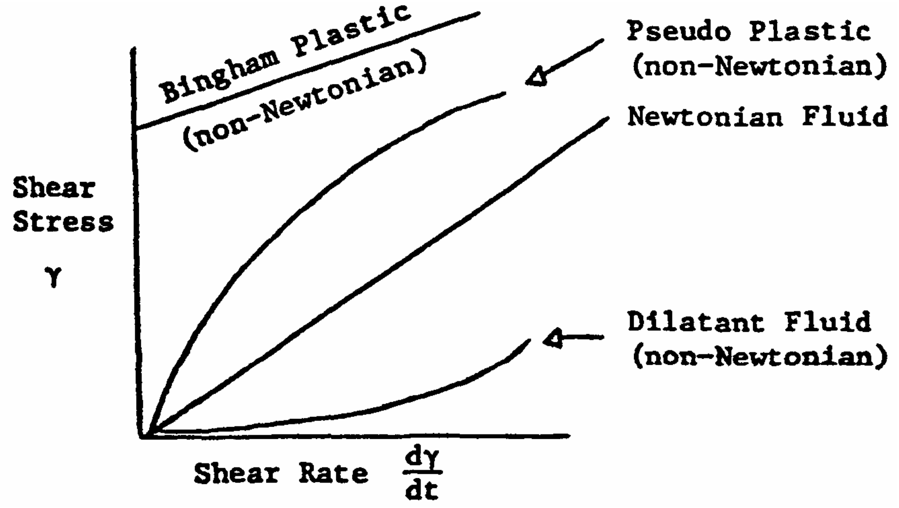


Figure 6.1: Newtonian and Non-Newtonian Fluid Properties

Another way to show the difference between Newtonian and non-Newtonian fluids is to plot the viscosity versus the shear rate as shown in Figure 6.2. For Newtonian fluid, the viscosity "μ" is a constant at a set temperature while for a non-Newtonian, it is not.

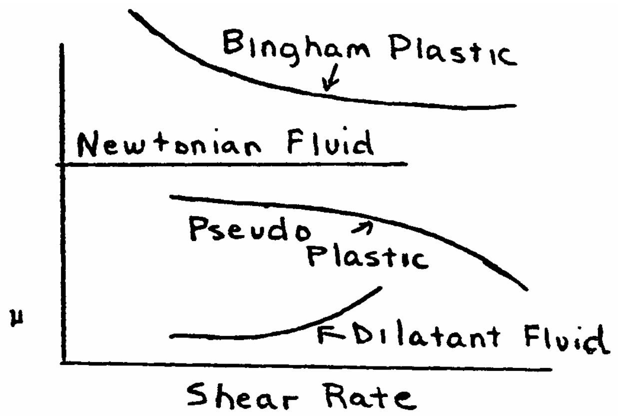


Figure 6.2: Newtonian and Non-Newtonian Fluid Viscosities

6.1.3 Other Comments

We also wil limit ourselves to systems in which the fluid is a continuous substance, ie. we are not considering systems in which there are only a few molecules present as different laws apply, (high vacuum, etc.).

6.1.4 Definitions

Let us define some common physical properties of a fluid:

Density

ρ = mass of substance per unit volume, normally lbs/cu.ft., (kg/m^3).

Viscosity

μ = a particular fluid property. It is the internal friction in a fluid that reduces flow. It is defined as:

$$\mu = \frac{ShearingStress}{Rate\ of\ \ Shearing\ Strain}$$

Or we can consider the following diagram:

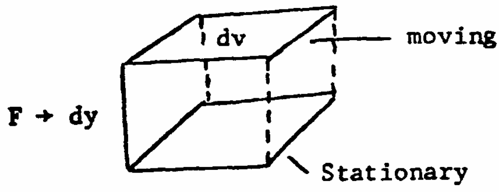


Figure 6.3: Physical Properties of Fluid

The Force (F) per unit area (A) applied to make the top layer move at a velocity (dv) a distance (dy) from the stationary plane can be expressed by the following equation:

Equation 6-1

$$\frac{F}{A} = \mu \frac{dv}{dy} \quad or \quad = \mu \frac{d\gamma}{dt}$$

where:

μ = the viscosity of the fluid

y = shear stress

t = time

This property has the dimensions of $\frac{mass}{\text{length - time}}$ and is normally expressed as centipoise in the metric system. There are many other units that viscosity is expressed in due to the variety of means of measuring it, ie. Saybolt, Kinematic, Engler, etc.

Reynolds Number

Another well known item concerned with. fluids is the Reynolds number. This is defined as follows.

Equation 6-2

$$\mathrm{Re} = \frac{(Diameter\ of\ Pipe)(Velocity\ of\ fluid)(Density\ of\ fluid)}{Viscosity\ of\ fluid} = \frac{D\,v\,\rho}{\mu}$$

The Reynolds Number is important as it defines the fluid in a system, because fluids that have the same Reynolds Number are dynamically similar and when applied to geometrically similar systems, they behave identically. For example, the friction factor "f" is correlated against the Reynolds Number.

6.1.5 Symbols

In the course of this section we will be using many symbols. The main ones are as follows, along with the common units:

F = Force (lbs normally) [Newton]

ρ = Density (lbs/cu.ft.) [kg/m^3]

μ = Viscosity ($\frac{lbs}{ft\ x\ \sec}$) [or in poises or $\frac{kg}{m - \sec}$]

D = Pipe diameter (ft) [m]

d = pipe diameter (in) [cm or mm]

v = Velocity (ft/sec) [m/sec]

G = Mass velocity (lbs/ft^{2}sec) [kg/m^2/sec]

g_c = Gravity (32.2 ft/sec^2) [980 cm/sec^2] note: sometimes has unit $\frac{ft}{hr^2}$

w = Work (BTUs or ft. lbs} [kilojoules]

q = Heat (BTUs or ft. lbs} [kilojoules]

Q = Flow (SCFH or SCFD) [m^3/Hr or m^3/day]

z = Height or Potential (ft) [m]

Z = Compressibility Factor

u = Internal Energy (BTUs or ft. lbs) [kilojoules]

L = Length of pipe (ft or miles) [m]

W = Mass flow $\frac{lb}{\sec}\left[\frac{kg}{se}\right]$

A = Cross-sectional area (ft^2) [m^2]

V = Volume (normally specific volume, cu.ft./lb) [m^3/kg]

P = Pressure (normally psi) [kpa]

T = Temperature (normally in °R) [°K]

S = Gas gravity compared to air = 1.0

6.2 Energy Equations

6.2.1 The Drag Law

Whenever a fluid flows past a solid object or a solid object passes through a fluid, a force "F" is required to overcome the friction developed. This can be expressed by the equation:

Equation 6-3

$$F = \frac{f'\rho A v^2}{2g_c}$$

where:

A = the area of the solid in contact with the fluid.

f' = the factor dependent only on Reynolds Number for the system.

V = the velocity of the fluid.

g_c = the gravity.

ρ = the density of the fluid.

6.2.2 Energy Equation

Consider the following system for 1 lb. (or 1 kilogram) of material flowing:

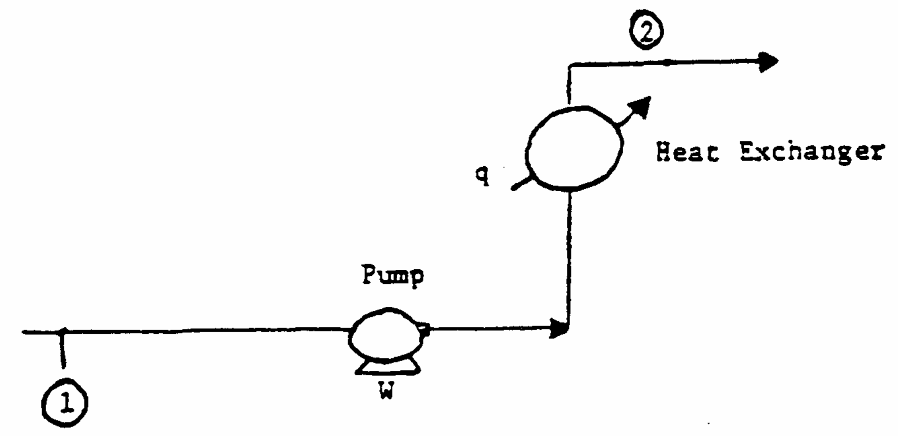


Figure 6.4: Material Flowing Through a Heat Exchanger

An energy equation can be written from Point 2 as compared to Point 1.

Equation 6-4

$$u_2 + \frac{v_2^2}{2g_c} + z_2 + P_2V_2 = u_1 + \frac{v_1^2}{2g_c} + z_1 + P_1V_1 + q + w$$

or

Equation 6-5

$$\Delta u + \Delta\left(\frac{v^2}{2g_c}\right) + \Delta z + PV = q + w$$

Let ℓw = lost work (work to overcome friction or other changes). This would be part of the term "w" in (5) above. However, let us consider the case where no outside work occurs. We will also consider the case in which there is no outside heat. Equation (5) reduces to

Equation 6-6

$$\int_1^2 VdP + \Delta\left(\frac{v^2}{2g_c}\right) + \Delta z + lw$$

For an incompressible fluid this can be expressed as:

Equation 6-7

$$\frac{\Delta P}{\rho} + \Delta\left(\frac{v^2}{2g_c}\right) + \Delta z = lw$$

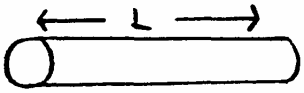
6.2.3 Basic Equation for Incompressible Flow

Equation (7) can be used to develop the Fanning Equation or the Darcy Equation for flow in pipes. Let us consider the Drag Equation for flow in pipes where F (force) is required to overcome friction.

Equation 6-8

$$F' = f'\frac{\rho \pi D L v^2}{2g_c}$$

The area is πDL.



Assume that the fluid moves a distance dL then the energy lost in ft. lbs. is FdL. This is equal to the lost work, ℓw. Now the mass of fluid moved is equal to:

$$\frac{\rho \pi D^2 dL}{4}$$

or ℓw per unit mass of fluid is expressed as follows:

Equation 6-9

$$lw = \frac{F'dL}{\rho \pi D^2 dL \big/ 4} = \frac{4F'}{\rho \pi D^2}$$

Now, replacing F' from (8) we have:

Equation 6-10

$$lw = \frac{2f'Lv^2}{Dg_c}$$

Now substitute in the energy equation for a non-compressible fluid in which there is no change in elevation or potential energy or change in velocity. (Equation (7) modified).

Equation 6-11

$$lw = \frac{\Delta P}{\rho} = \frac{2f'Lv^2}{Dg_c}$$

This is a form of the Fanning Equation.

Now let $f = 4f' \quad f' = \frac{fm}{4}$

We can now express the pressure loss in the familiar Darcy Equation where "f" is the regular friction factor. (Moody Friction factor)

Equation 6-12

$$\Delta P = \frac{fm \rho L v^2}{2g_c D} \qquad in\ {}^{lb}\!\big/_{ft^2}$$

or the Darcy Equation in lbs/in^2

Equation 6-13

$$\Delta P = \frac{\rho \, fm \, L v^2}{144 \, D \left(2 g_c\right)}$$

Note: The friction factor is sometimes expressed as the Fanning Friction - Factor ff which is ¼ of fm.

6.2.4 Friction Factor

The friction factor has been correlated vs Reynolds Number. In Figure 6.5, this so called Moody diagram gives different values for different types of flow. These types of flow are listed below:

Laminar Flow

A flow in which fluid flows in straight lines, occurs below Re. = 2000

Transition Range

Between Re. = 2000 to 4000

Turbulent Flow

Above Re. = 4000. We normally have this type of flow.

Note: The roughness of pipe affects the friction factor. (Does not drop very fast with increasing Re. No. in rough pipe). This is the value ε/D shown in Figure 6.5 and 6.8.

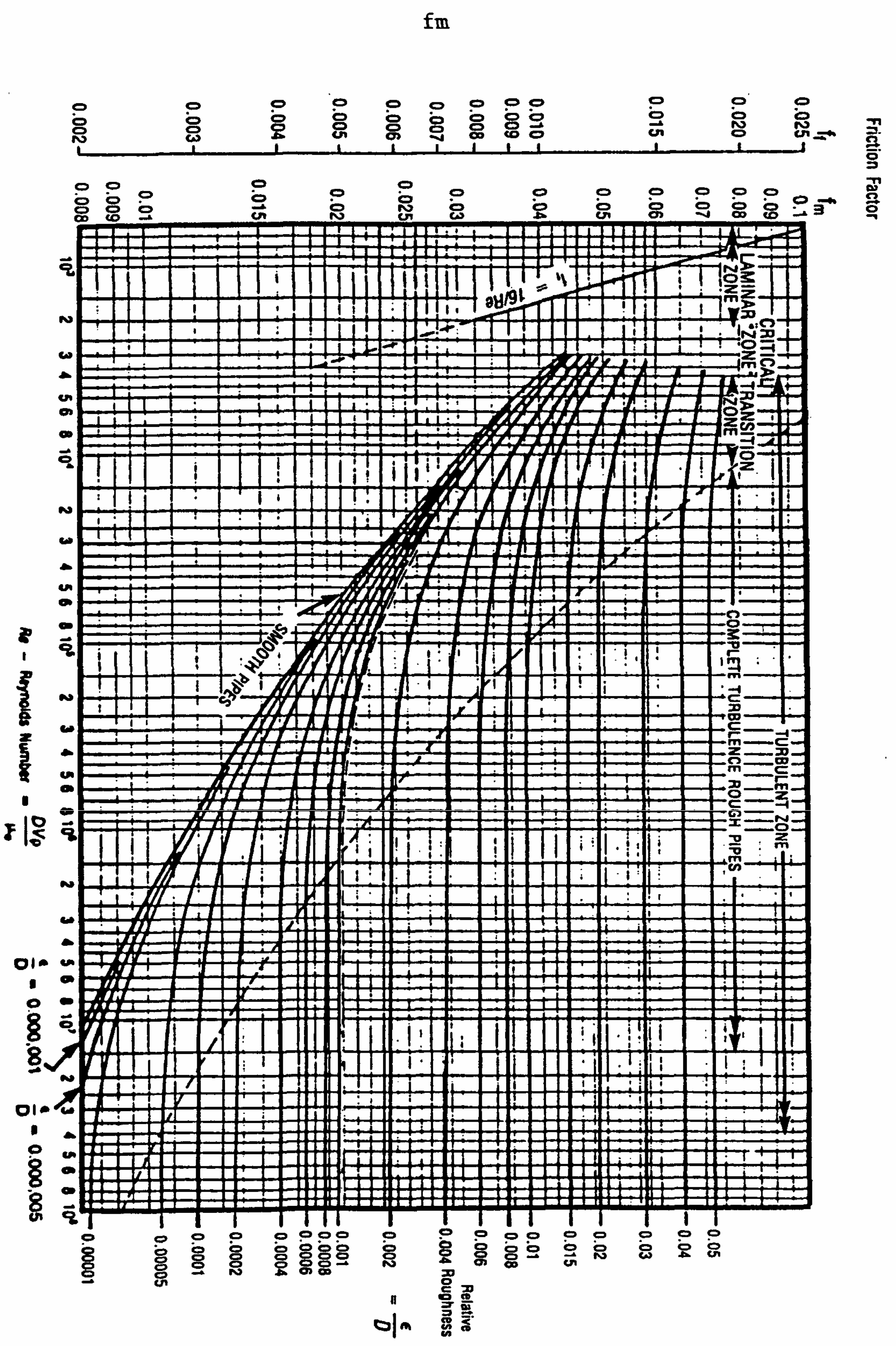


Figure 6.5: Friction Factors for Commercial Pipe

6.2.5 Flow Pattern in Pipe

Let us consider flow patterns in pipe. Figure 6.6 shows some typical flow patterns.

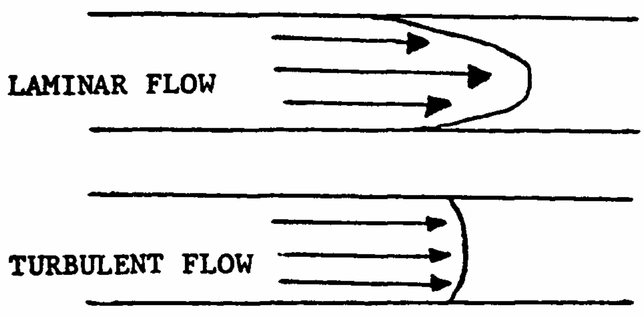


Figure 6.6: Flow Patterns in Pipe

This can be contrasted if the ratio of the average velocity "v" divided by v_{max} is plotted against Re. Number.

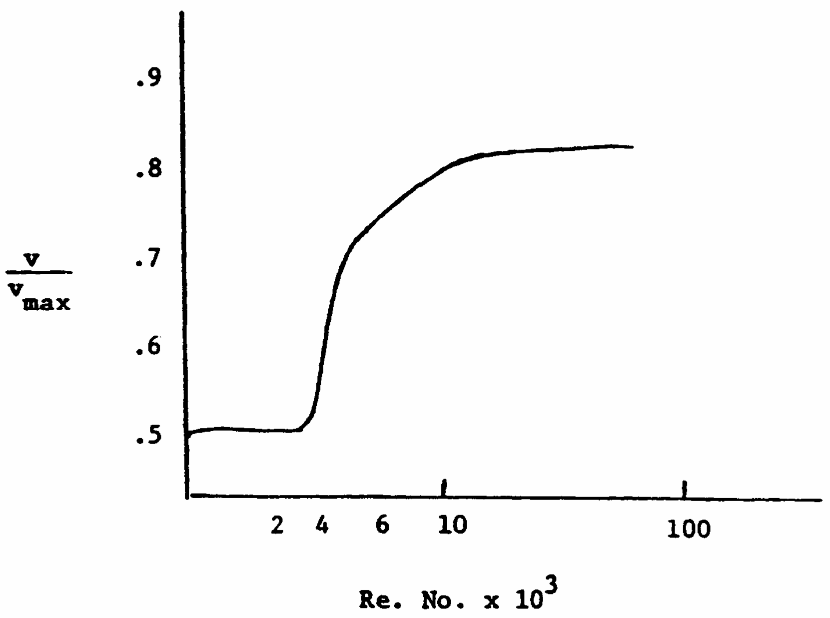


Figure 6.7: Velocity Profile vs Reynolds Number

6.3 Liquid Flow

We are concerned primarily with the flow of liquids in pipes and will not discuss flow over weirs or in channels. There are many formulas giving the pressure drop in pipes. In GPSA Data Book on pages 10-10 and 10-11 charts these are giving pressure drops in psi/l00 ft. Also data in kpa/l00 m are given in the SI GPSA Data Book on the same page number.

A good basic formula that can be used is the Darcy-Wiesbach formula (for turbulent flow).

Equation 6-14

$$\Delta P = \frac{fW^2 L}{5715 \rho D^5}$$

where:

ΔP = pressure drop psi

f = friction factor from Colebrook-White chart (Figure 6.8 or Figure 6.5). (fm - Moody Value)

W = Flow, lbs/sec.

ρ = density, lbs/cu.ft.

D = inside diameter in ft.

L = length in feet.

As can be seen from Figure 6.8, "f" is a function of the Re. No. and the roughness factor "e" and thus e/D.

If we have laminar flow, we can find "f" from the Hagen-Poiseuille Law which is:

Equation 6-15

$$f = \frac{64}{\text{Re}}$$

where:

Re = the Reynolds Number.

Another way of obtaining the pressure drop is to use the data as given in the Ingersoll Rand's "Cameron Hydraulic Data" in which the pressure drop (head loss) for various sizes of pipe is given for water and HC fluids against a viscosity. This is also reproduced in Ludwig, Vol. I, P.78.

Because of the complexity of elbows, tees, valves, etc., it is not possible or correct to just take the straight length of pipe. All fittings have to be taken into account, thus an equivalent length is calculated. This is straight length plus equivalent length of fittings as determined from Fig. 10-14, GPSA Data Book.

If you do not have the actual number of elbows, tees, etc., use at least 20% of straight length pipe in process plants and 10% for pipelines.

We have been concerned with measuring pressure drop. Actually prime concern is to determine the most economic size. This is a balance between pressure drop and power required for pumping, as is shown in Figure 6.9.

This optimum size has been worked out for several conditions. The following table gives some economic velocities. This table applies primarily to pump and compressor discharge piping.

Table 6.1: Recommended Velocities in Pipe

Fluid Density		**Optimum Velocity**	
lbs/cu.ft.	**kg/m^3**	**ft/sec**	**m/sec**
100	(16.018)	5.1 - 8.0	(1.55 - 2.43)
50	(8.009)	6.2 - 10.0	(1.9 - 3.05
10	(1.602)	10 - 16	(3.05 - 4.87)

1	(0.160)	19.5 - 31	(5.94 - 9.5)
0.1	(0.016)	39 - 59	(11.9 - 18.0)
0.01	(0.0016)	78 - 112	(23.8 - 34.2)

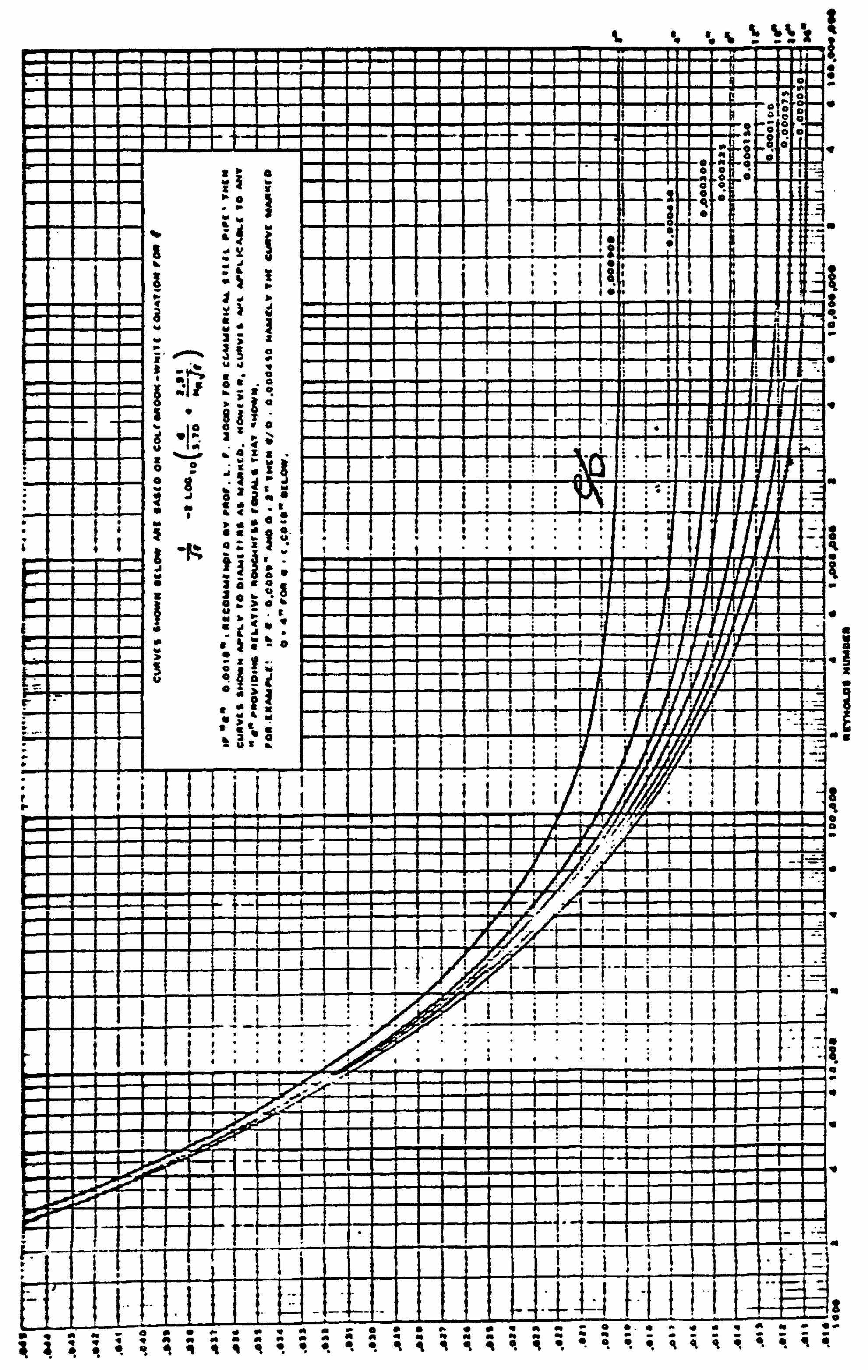


Figure 6.8: Friction Factor VS Reynolds Number

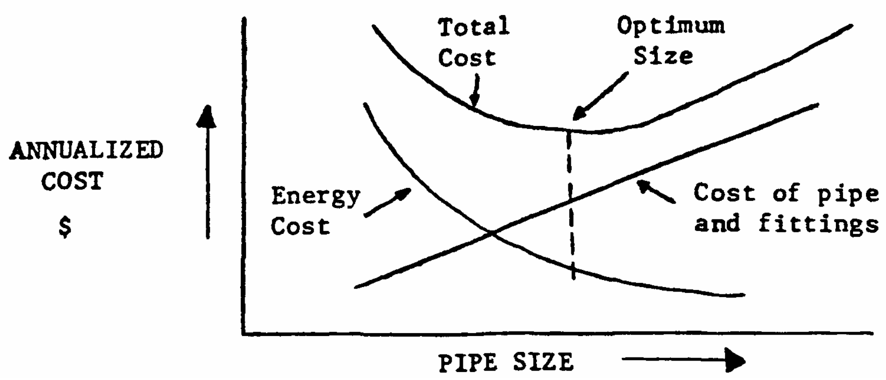


Figure 6.9: Optimum Pipe Size Determination

This data can also be expressed more specifically for particular services as follows:

Suggested Allowable Velocities or Pressure Drops in Process Plants

The following data is to be used as a guide. A thorough review of the actual installation should always be made.

Table 6.2: Liquids - Allowable Velocities

	ft/sec		
	Boiling Liquids	**Light Hydrocarbons and Water**	**Viscous Oil, Etc.**
Pump Discharge	5 - 8	5 - 8	3 - 5
Pump Suction	1 (max)	3 (max)	1 (max)
Gravity Flow	0.5 *	2.5 *	1 – 2 *
	meters/sec		
	Boiling Liquids	**Light Hydrocarbons and Water**	**Viscous Oil, Etc.**
Pump Discharge	1.5 – 2.4	1.5 – 2.4	0.9 – 1.5
Pump Suction	0.3 (max)	1 (max)	0.3 (max)
Gravity Flow	0.15 *	0.8 *	0.3 – 0.6 *

* Should check on the pressure drop available basis also.

Table 6.3: Gases - Allowable Velocities

	ft/sec	**m/sec**
Pressure (atmospheric)	80 – 100	24.4 - 30.4
100 psig	60 – 80	18.3 - 24.4
200 psig	50 – 60	15.2 - 18.3
300 psig	40 – 50	12.2 - 15.2
500 psig	30 – 40	9.1 - 12.2
1000 psig	10 – 20	3.05 - 6.1
Compressor Suction	30	9.1
Compressor Discharge	70	21.3

Table 6.4: Vacuum Systems - Allowable Pressure Drop

Vacuum	psi/100 ft
28" of Mercury	0.05
25" of Mercury	0.10
15" of Mercury	0.15

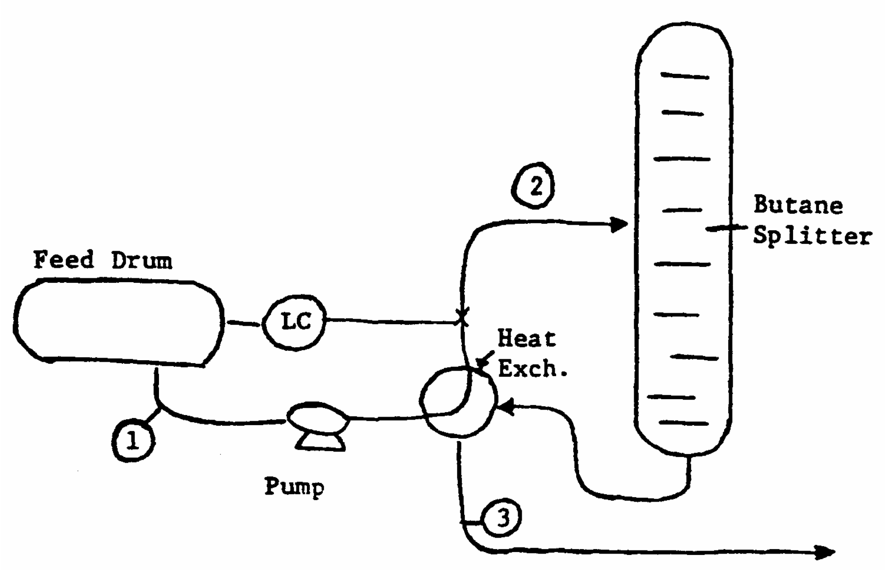
Table 6.5: Steam Systems - Allowable Pressure Drop

Steam Pressure PSIG	PSI/100 ft
10 – 50	0.5
50 - 500	1.0
500 and greater	1.5

The problem of long transmission lines is slightly different. Since the cost of pump stations is higher than pumps alone, higher velocities probably can be used. However, an economic balance equation should be developed. For rough sizing about 6 to 10 psi per mile can be used. Also, pump stations are usually located every 100 miles or less. However, this is a balance. Pump discharge pressure is normal maximum for pipe, i.e. 1440 psig (10,024 KPa) or 720 psig (5065 KPa) depending on the flange rating of the valves in the system.

Example Problem 6.1

You are to size the butane splitter feed and bottoms piping from the feed drum to the tower as shown by the sketch below.



Solution

Line No.	Flow (Usgpm)	Service	Allowable Velocity (ft/sec)	Size (inches)	Pressure Drop (Psi/100 ft)	Velocity (ft/sec)	Comments
1	234	Pump Suction	1	10	0.02	0.9	
2	234	Pump Discharge	5 - 8	4	0.75	6	
3	146	Rundown to Storage	5 - 8	3	1.2	6	*

* Should check length of line and available pressure drop. It may be that 4 inches is best.

Line No.	Flow (m^3/hr)	Service	Allowable Velocity (m/sec)	Size (mm)	Pressure Drop (kpa/100 m)
1	53.14	Pump Suction	0.3	254	2
2	53.14	Pump Discharge	1.5 – 2.4	101.2	30
3	33.16	Rundown to Storage	1.5 – 2.4	75	45

Control Valves

Another item to consider is control valve sizing. Generally it is best to let a process control valve take about one third of the available pressure drop in the system.

6.4 Gas Flow

The flow of gas is complicated because it is compressible and the pV in the flow equation cannot be reduced to Vdp but the term pdV has to be considered also. This pdV term is, however, cancelled out in the general equation by a change in internal energy due to a change in pressure. We have to consider two types of flow:

Adiabatic Flow

Flow is an insulated pipe in which no heat is transferred. The gas law equation for this is:

Equation 6-16

$$Pv^k = Constant$$

or

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^k$$

where

$$k = \frac{C_P}{C_V}$$

Isothermal flow

The gas is kept at a constant temperature. The gas law equation for this condition is such that

Equation 6-17

$$\frac{P_2}{P_1} = \frac{V_1}{V_2}$$

Isothermal flow is usually taken for flow in long pipelines and formulas developed for flow in pipelines are usually based on isothermal flow. For flow through nozzles at high speeds, etc. adiabatic flow is considered.

6.4.1 Adiabatic Flow

Let us firsts consider adiabatic flow q = 0. Assume work = 0 and potential is zero, then

Equation 6-18

$$P_1V_1 = U_2 - U_1 + \frac{v_2^2 - v_1^2}{2g_c} + P_2V_2$$

Now

Equation 6-19

$$C_V\left(T_2 - T_1\right) = U_2 - U_1$$

and

Equation 6-20

$$PV = RT$$

also

Equation 6-21

$$C_V = \frac{R}{k-1}$$

where:

k is the ratio of specific heats.

Therefore

Equation 6-22

$$\frac{v_2^2 - v_1^2}{2g_c} = P_1V_1 - P_2V_2 + C_V\left(T_1 - T_2\right)$$

Equation 6-23

$$\frac{v_2^2 - v_1^2}{2g_c} = P_1V_1 - P_2V_2 + \frac{P_1V_1}{k-1} - \frac{P_2V_2}{k-1}$$

or

Equation 6-24

$$\frac{v_2^2 - v_1^2}{2g_c} = \frac{k}{k-1}\left(P_1V_1 - P_2V_2\right)$$

Now, for adiabatic reversible flow

Equation 6-25

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^k = \left(\frac{\rho_2}{\rho_1}\right)^k$$

Equation (24) becomes

Equation 6-26

$$\frac{v_2^2 - v_1^2}{2g_c} = \left(\frac{k}{k-1}\right)\left(\frac{P_1}{\rho_1}\right)\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}\right]$$

We can use this equation for gas flow through nozzles, orifices, flow meters. For example, if W is the weight of gas passing through a nozzle, W at the throat of a nozzle

Equation 6-27

$$W = \frac{A_2 v_2}{V_2}$$

and assuming v_1^2 is small, we obtain

Equation 6-28

$$W = A\sqrt{\left(\frac{2kg_c}{k-1}\right)\left(\frac{P_1}{V_1}\right)\left(\frac{P_2}{P_1}\right)^{\frac{2}{k}} - \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}}$$

If plot of W versus $\frac{P_2}{P_1}$ is made we will get a plot as is shown in Figure 6.10.

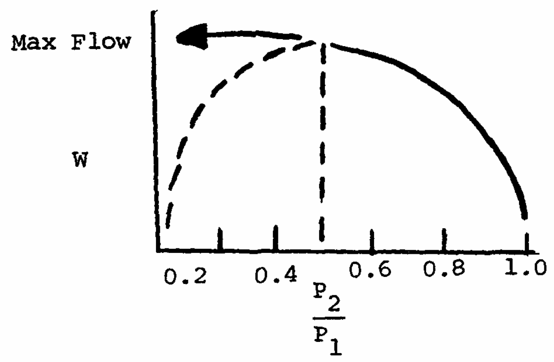


Figure 6.10: Maximum Flow of Compressible Fluid

The maximum rate of flow can be found by differentiating W with respect to P_2 and settling result to 0. Call P_2 at this condition P_c.

Equation 6-29

$$\frac{P_c}{P_1} = \left(\frac{2}{k+1}\right)^{\frac{1}{k-1}}$$

The velocity at this point can be shown to be:

Equation 6-30

$$v_c = \sqrt{\frac{2g_c}{k+1}k\left(P_1V_1\right)} = \sqrt{\frac{kP_c}{\rho_c}}$$

or, in English units

Equation 6-31

$$v_c = \sqrt{kg_cT_c\frac{z_cR}{M}}$$

which is the velocity of sound at the critical pressure.

where:

v_c = velocity of sound, ft/sec

g_c = gravity, 32.2 ft/sec^2

R = 1541 ft.lbs/mole

M = mole weight of gas in lbs

Z_c = compressibility factor at outlet conditions or when velocity reaches that of sound.

T_c = Temperature when gas is at velocity of sound or at pressure P_c in °R.

Note: The velocity of sound is the maximum velocity that can occur in gas pipes. This occurs at end of pipe. A reduction of the pressure below the value of P_c or when $P_2 < 0.5\ P_1$ will not increase the flow.

Field flare stacks are sometimes sized for close to sonic velocities when the maximum amount of gases are being flared. (Usually 0.8 of sonic velocity). Plant flare stacks are sized at lower sonic velocities, about 0.2 of sonic velocities. This lower value is necessary as higher than 0.2 can often cause blow out of a flame.

6.4.2 Isothermal Flow

Next let us consider isothermal flow which, is the normal flow in most gas gathering lines, pipelines, etc. If we assume:

1. No mechanical work in system
2. Have horizontal flow.

we can write the general energy equation in the following form:

Equation 6-32

$$VdP + \frac{d\left(v^2\right)}{2g_c} + dR = 0$$

Change in pressure + Change in velocity + Lost work to overcome friction = 0

Now

$$dR = \frac{fv^2dl}{2g_cD}$$

(This is the drag law)

where:

ℓ = length of line.

Equation becomes:

Equation 6-33

$$VdP + \frac{vdV}{g_c} + \frac{fv^2dl}{2g_cD} = 0$$

or

Equation 6-34

$$\frac{2g_cVdP}{v^2} + \frac{2dv}{v} + \frac{fdl}{D} = 0$$

Integrating this equation between points 1 and 2 we obtain:

Equation 6-35

$$P_1^2 - P_2^2 = \frac{v_1^2P_1}{g_cV_1}\left[2\ln\frac{v_2}{v_1} + \frac{fl}{D}\right]$$

or if we neglect the acceleration or kinetic energy change we can obtain the equation for long pipes

$$\frac{fl}{D} >> 2\ln\frac{v_2}{v_1}$$

Equation 6-36

$$\frac{P_1^2 - P_2^2}{P_1^2} = \frac{flv_1^2}{g_cD_1P_1V_1}$$

or

Equation 6-37

$$P_1 - P_2 = P_1\left[1 - \sqrt{1 - \frac{flv_1^2}{g_c D P_1 V_1}}\right]$$

6.4.3 Common Formula for Gas Flow

We can change the above equation to units in which we have a friction factor and common units. A typical equation that covers all cases for horizontal flow:

Equation 6-38

$$Q = K\frac{T_s}{P_s}\left[\frac{\left(P_1^2 - P_2^2\right)d^5}{fLSTZ_a}\right]^{\frac{1}{2}}$$

where:

	English Units	**Metric Units**
Q - Flow in	SCFD	m^3/D
P - Pressure in	psia	$bars = \frac{kPa}{100}$
P_s - Pressure base in	psia	$bars = \frac{kPa}{100}$
T_s - Temperature base in	°R	°K
T - Operating temperature in	°R	°K
d - Pipe diameter in	inches	cm
L - Pipe length in	miles	km
S - gas specific gravity	----	----
Za - average compressibility between that at P_1 and P_2	----	----
f - Friction factor	See Figure 6.11	----
k	38.77	0.1842

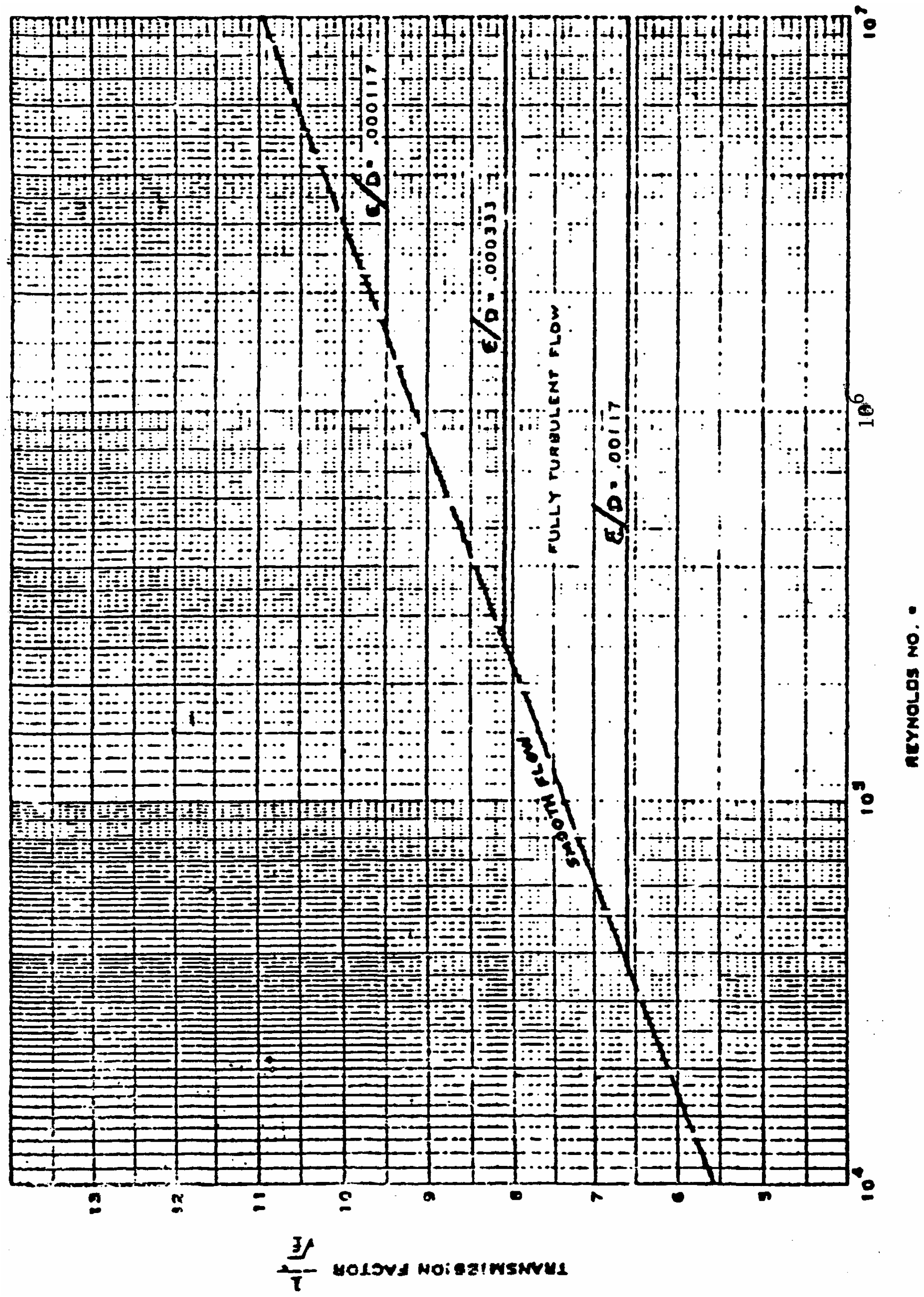


Figure 6.11: Recommended Friction Factors for Gas Flow

A short discussion of finding $\frac{1}{f}$ is desirable. The factor is correlated against the Re. No. and $\frac{\varepsilon}{D}$, the roughness factor. ε is the height of the roughness in inches and D is the diameter in inches - (Or these could be in cm). Here are some roughness data.

Table 6.6: Roughness Data

Low Pressure	**Pipe Size**	ε
(4"-10" of H_9 Vacuum)	2 - 8	0.01"
(100 – 250 mm of H_9)	8 - 30	0.007"
Med. Pressure		
(2 - 10 psig)	All	0.0025”
(15 - 170 kpa)	All	0.0025”
High Pressure		
(>10 psig)	All	0.0025”
(170 kpa)	All	0.0025”
New Pipe	All	0.0007"
5 yrs old	All	0.002"
10 yrs old	All	0.0025
15 yrs old	All	0.003"

There are some other well known empirical formulas. In these the friction factor is expressed as a function of either the Diameter (Weymouth) or the Re. No. (Panhandle).

The Weymouth formula which is often used assumes that $\frac{1}{f}$ is a function of the diameter "d".

That is:

$$f = \frac{0.032}{d^{\frac{1}{3}}}$$

The formula is:

$$Q = 433.5 \frac{T_b}{P_b} \left[\frac{P_1^2 - P_2^2}{STLZ_a} \right]^{\frac{1}{2}} d^{2.667}$$

or S.I.

Equation 6-39

$$Q = 0.0037 \frac{T_b}{P_b} \left[\frac{P_1^2 - P_2^2}{STLZ_a} \right]^{\frac{1}{2}} d^{2.667}$$

where:

d = pipe diameter in inches (mm)

L = line length in miles (If L in feet constant is (km) 30,490 instead of 433.5)

P_1, P_2 = pressure in psia at points 1 and 2

Q = SCFD at T_b and P_b (m^3/d)

S = specific gravity

T = °R (°K)

T_b = base temp °R (°K)

P_b = base pressure, psia (Kpa)

Charts in the GPSA Data Book plot (Page 10-3) plot flows vs $P_1^2 - P_2^2 / km$ and pipe sizes for the formula. The Weymouth formula is usually used for sizing gathering lines.

Another common formula is the Panhandle. Here the friction factor is taken as:

$$\frac{1}{f} = \theta(\mathrm{Re})^{0.73}$$

This formula is given on the following pages. Please note that E is the pipeline efficiency 0.92 for clean transmission lines and 0.88 for gathering lines.

Note: E is the pipeline efficiency usually it is taken as 0.92, but can vary from 0.85 to 0.95 depending on operating conditions.

6.4.3.1 Summary of Equations for Single Phase Gas Pipelines Using One-Step Calculation Procedure

Capacity

General Equation

Equation 6-40

$$Q = KE\left(\frac{T_b}{P_b}\right)^{\alpha}\left(\frac{P_1^2 - P_2^2}{T_a L Z_a}\right)^{\beta}\frac{D^{\chi}}{S^{\nu}}$$

Equation	System of Units	K	α	β	γ	υ
Panhandle	Field	435.87	1.0788	0.5394	2.6182	0.4606
Panhandle	SI	4.596 x l0^{-3}	1.0788	0.5394	2.6182	0.4606
Panhandle Eastern	Field	737	1.02	0.510	2.530	0.490
Panhandle Eastern	SI	10.02 x l0^{-3}	1.02	0.510	2.530	0.490

Upstream and Downstream Pressures

General Equations

$$P_1 = \left\{ P_2^2 + K\left(\frac{Q}{E}\right)^{\alpha}\left(\frac{P_b}{T_b}\right)^{\beta}\frac{S^{\chi}}{D^{\nu}}T_a L Z_a \right\}^{1/2}$$

$$P_2 = \left\{ P_1^2 - K\left(\frac{Q}{E}\right)^{\alpha}\left(\frac{P_b}{T_b}\right)^{\beta}\frac{S^{\chi}}{D^{\nu}}T_a L Z_a \right\}^{1/2}$$

Equation	System of Units	K	α	β	γ	υ
Panhandle	Field	1.279 x 10^{-5}	1.8539	2	0.8539	4.8539
Panhandle	SI	2.157 x 10^{4}	1.8539	2	0.8539	4.8539
Panhandle Eastern	Field	2.385 x 10^{-6}	1.9608	2	0.9608	4.9608
Panhandle Eastern	SI	8.315 x 10^{3}	1.9608	2	0.9608	4.9608

Diameter

General Equation

$$D = K\left(\frac{Q}{E}\right)^{\alpha}\left(\frac{P_b}{T_b}\right)^{\beta}\left(\frac{T_a L Z_a}{P_1^2 - P_2^2}\right)^{\chi}\frac{S}{1}$$

Equation	System of Units	K	α	β	γ	υ
Panhandle	Field	0.0982	0.3819	0.4120	0.2060	0.1759
Panhandle	SI	7.8133	0.3819	0.4120	0.2060	0.1759
Panhandle Eastern	Field	0.0736	0.3953	0.4032	0.2016	0.1937
Panhandle Eastern	SI	6.1684	0.3953	0.4032	0.2016	0.1937

Definition of Parameters and Units

Parameter	Definition	Units	
		Field	SI
D	Inside diameter of pipe.	inch	mm
E	Pipeline efficiency factor, expressed as a fraction	----	----
S	gas gravity relative to air = 1	----	----
L	total length of pipeline	mile	km
P_b	reference pressure for standard conditions	psia	kPa
P_1	upstream pressure	psia	kPa
P_2	downstream pressure	psia	kPa
Q	gas flow rate at standard conditions	ft^3/day at T_b, P_b	m^3/day at T_b, P_b
T_b	reference temperature for standard conditions	°R	°K
T_a	average temperature of the flowing gas	°R	°K

Z_a	average compressibility factor of the flowing gas	----	----

When there is a significant difference in head between the start and finish of a transmission loss the change of potential energy Δz must be taken into account. This can be done by the use of the following equation:

Equation 6-41

$$\frac{\Delta z\, S}{A T_a Z_a} = \frac{\ln P_1}{P_2}$$

where:

	English Units	Metric Units
Δz = head difference	ft	m
S = gas gravity	----	----
T_a = ave temperature	°R	°K
Z_a = ave compressibility	----	----
P_1 = Pressure at 1	psia	$\frac{kpa}{100}$
P_2 = Pressure at 2	psia	$\frac{kpa}{100}$
A = Constant	54.34	29.28

When sizing short process lines in vapour service the following formula can be used:

Equation 6-42

$$\Delta P_{100} = \frac{W^2}{e}\left(\frac{0.000336 f_f}{d^5}\right)$$

where:

ΔP_{100} = Pressure drop/l00 ft

f_f = Fanning friction factor

W = Flow lbs/hr

ρ = density lbs/cu.ft.

d = diameter in inches

See GPSA Data book page 10-5 and 10-6 for solving this formula,

or in metric units:

$$\frac{\Delta P}{100M} = \frac{W^2}{\rho}\left(\frac{62530\,x\,10^2 f}{d^5}\right)$$

where:

ΔP = kpa

f = Fanning Friction Factor

W = Flow kg/hr

d = inside diameter in mm

ρ = density $\frac{kg}{m^3}$

6.4.4 Line Sizing

The prime problem is to determine what size to make pipe for carrying gas. This again is an economic balance. The general data given in the table on optimum velocity can be given or the more detailed data given previously in Table 6.3: Gases - Allowable Velocities can be used.

6.4.5 Gathering Pipelines

For gathering lines from wells to a processing facility, etc. we have a different problem. The well initially can be at a very high pressure - 3000 to 5000 psig (20,684 to 34,473 kpa) depending on depth. It is necessary to do a study of the maximum pressure in the pipeline vs well deliverability vs wall thickness, etc. Usually the maximum pressure allowable in the line is 1440 psig, (about 10024 kpa) which is the maximum pressure rating for 600 ANSI raised face and ring joint flanges. There are, of course varying other pressures used depending on special circumstances, such as recycling, etc. For pressure drops varying values are used. They are affected by the length of the line, etc. About 10 - 50 psi/mile is sometimes used.

Also, if wellhead pressure is set by pipe flange considerations and the processing facility outlet condition is set by the transmission company (usually 900 psig) then the allowable and available pressure drop is set. Example Problem 2 in Chapter 14 shows how a gathering system is sized.

6.4.6 Gas Transmission

To size gas transmission lines a different set of conditions have to be reviewed. A detailed study of pipe diameter versus compressor HP has to be made after the design volumes for both initial and future conditions have been determined. Some of the factors considered and the rules of thumb for initial design are:

1. Design pressure limitation - either 600 ANSI rating or 400 ANSI rating valves, flanges, etc., are used, usually 400.
2. The optimum compression ratio of generally taken as:
    - for reciprocating machines - 1.3 to 1.5.
    - centrifugal machines - 1.2 to 1.3.
3. The spacing of compressor stations is:

  - reciprocating machines – 80 - 100 miles apart.
  - centrifugal machines – 40 - 50 miles apart.
4. The pressure drop used is 5 - 15 psi per mile.
5. The ease of installing the pipe.
6. The place where looping will be done.
7. The storage of gas required.

6.4.7 Steam

Another fluid to be considered is steam flow. This is also a compressible fluid and the general flow equations could be used. However, a specific formula for saturated and superheated steam has been developed along with nomographs. Generally it is desirable to keep the pressure drop in steam lines low so as to prevent condensation. (See Fig. 10-10 in the GPSA Data Book for determining pressure drop in steam lines). For steam lines the following allowable pressure drops are often used:

- 1 lb/100 ft for 50 to 500 psig systems.
- About 0.5 psig for 50 psig systems or lower pressures.
- For pressures above 500 psig, use 1.5 lbs/100 ft.

In terms of velocities, the following are often used:

- 20 psig - 100 ft/sec
- 150 psig - 130 ft/sec

In steam condensate systems, make sure the pressure drop is low, ie. about 0.5 psi per 100 ft.

6.5 Two Phase Flow

6.5.1 General

The next consideration is two phase flow. We are concerned with the flow of gas and liquids only. Flows of gases and solids such as occur in cat crackers or slurry flows do not concern us.

Two phase flow occurs quite commonly in gathering lines from wells to a processing facility. It is possible to separate at the wellhead and have a gas line and liquid line. However, even this does not solve the problem as retrograde condensation can cause liquid to form in the gas line and lowering of pressure can cause the liquid to vaporize.

What are some of the problems with two phase flow?

1. Gas and liquid tend to separate in the pipe and gas flows are 2 to 10 times faster than the liquid and thus leaves the liquid behind. There is a drag on the interface between the phases and roughness on surface. This consumes energy and causes increased pressure drop.
2. Liquid accumulates in valleys and thus increases pressure required to flow fluid.
3. Two phase lines are very unstable and have widely varying pressure drops. A change in flow rate causes a line to unload liquid or to accumulate it, thus the phenomenon of

slugging. A two phase line is actually a pipeline system that is an extremely long storage tank.

The total pressure drop in a two phase flow system is often expressed by the equation:

Equation 6-43

$$\Delta P_{total} = \Delta P_{two\ phase\ flow} + \Delta P_{elevation\ change} + \Delta P_{acceleration\ change}$$

The most important pressure drop considerations are the $\Delta P_{two\ phase\ flow}$ and the $\Delta P_{elevation\ difference}$. The pressure drop due to an acceleration change is usually neglected as was discussed when considering the equation for isothermal gas flow (See equation (35)).

6.5.2 Types of Flow

Let us review the various types of flow. Figure 6.12 shows several of the types of flow to be expected. For horizontal flow we can have:

1. Bubble Flow - In this, gas bubbles move along the upper section of the pipe at about the same velocity as the liquid. This is the same as froth flow in which the entire pipe is filled with a froth.
2. Plug Flow - In this flow there are alternating plugs of gas and liquid which move along the upper section of the pipe. The lower section is liquid.
3. Stratified Flow - Flow in which liquid flows along the bottom and gas along the top of the pipe.
4. Wave Flow - This is similar to stratified flow except that gas flows at high velocities and disturbs the interface so that waves are formed which travel in the direction of flow.
5. Slug Flow - A slug of liquid is formed from a wave and moves at much greater than normal velocity.
6. Annular Flow - Liquid forms a film around the pipe wall and gas flows at a higher velocity down the centre.
7. Spray or Dispersed Flow - In this flow, the liquid is entrained in minute drops and is dispersed throughout the gas.

A good review of two phase flow is an article by R. Kern.1

6.5.3 Formulas for Various Types of Flow

The types of flow obtained under various conditions have been correlated as a function of the mass velocity "G" of the gas, the mass velocity of the liquid "L", the gas and liquid densities, the surface tension of the liquid and the viscosity of the liquid. Two parameters are used. They are:

Equation 6-44

$$\lambda = \left[\left(\frac{\rho_g}{0.075}\right)\left(\frac{\rho_L}{62.3}\right)\right]^{1/2}$$

and

Equation 6-45

$$\Psi = \frac{73}{\chi}\left[u_L\left(\frac{62.3}{\rho_L}\right)^2\right]^{1/3}$$

where:

γ = the surface tension of the liquid.

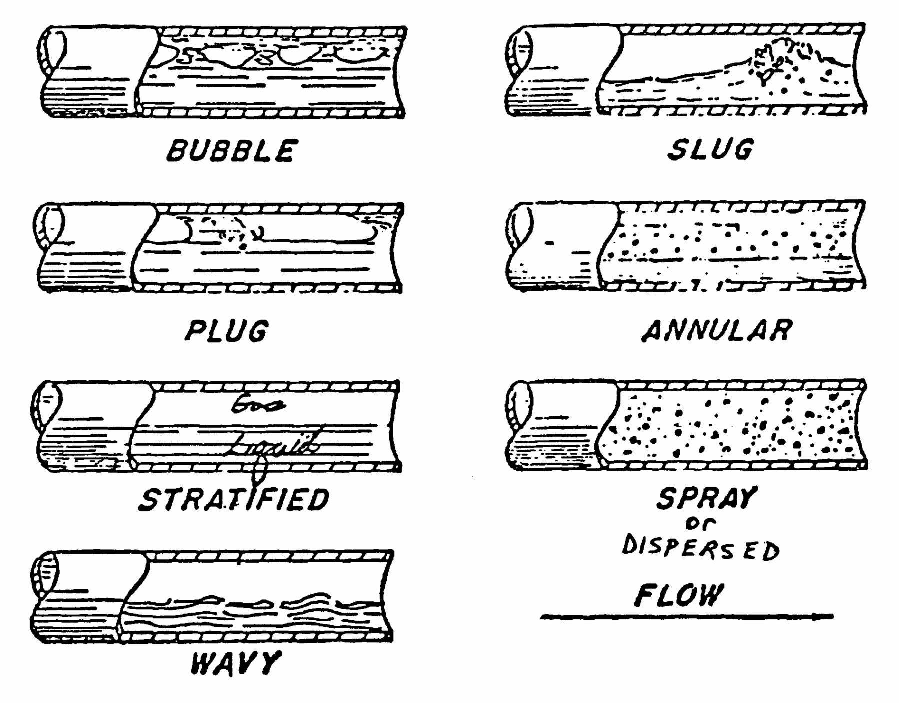


Figure 6.12: Two Phase Flow Pattern Sketches

Figure 6.14 correlates the type of flow versus functions relative to the above referred to parameter, i.e. $\frac{G}{\lambda}$ and $\frac{L\lambda\psi}{G}$. It will be noted that in increasing the gas flow, generally the type of flow goes from stratified flow to dispersed flow. When increasing liquid flow we go from stratified flow through slug or plug flow to bubble or froth flow.

Baker gives equations for each type of flow. These equations are formulas for the function $\theta^2{}_{GTT}$ where θ_{GTT} is the correction factor in the equation:

Equation 6-46

$$\Delta P_{TP} = \Delta P_G \phi_{GTT}^2$$

where:

ΔP_{TP} = pressure drop for two phases

ΔP_G = pressure drop for gas alone in total pipe

ΔP_L = pressure drop for liquid alone in total pipe

The pressure drop, when both phases are in the turbulent range for two phase flow, is equal to the pressure drop due to gas alone multiplied by the correction factor $\theta^2{}_{GTT}$.

All the equations are based on a factor x which equals $\left(\frac{\Delta P_L}{\Delta P_G}\right)^{\frac{1}{2}}$.

Froth or Bubble Flow

Equation 6-47

$$\phi_{GTT} = \frac{14.2\,x^{0.75}}{L^{0.1}}$$

Plug Flow

Equation 6-48

$$\phi_{GTT} = \frac{27.315\,x^{0.855}}{L^{0.17}}$$

Stratified Flow

Equation 6-49

$$\phi_{GTT} = \frac{15400\,x}{L^{0.8}}$$

Slug Flow

Equation 6-50

$$\phi_{GTT} = \frac{1190\,x^{0.815}}{L^{0.5}}$$

Annular Flow

Equation 6-51

$$\phi_{GTT} = (4.8 - 0.3125d)(X)^{0.343-0.021d}$$

Note: For Annular Flow only for up to 10" lines; above this, negative values are obtained, so use 10" for sizes larger than 10" as far as “d” is concerned.

For dispersed flow use data from Figure 6.13 based on the Lockhart-Martinelli correlation for two phase flow. x^2 is found and then the two phase flow pressure drop is found by going over to the curve and then up to the gas phase pressure drop.

For wave flow use graph of work of Schnieder, White and Huntington shown in Figure 6.15,

where:

"L" is the liquid mass flow, lb/hr/sq.ft. of total pipe cross sectional area.

"G" is the gas mass flow, lb/hr/sq.ft. of total pipe cross sectional area.

The term *x* can be found quite simply by considering the general liquid and gas flow equations and deleting the appropriate constants and symbols.

Equation 6-52

$$x^2 = \left(\frac{\Delta P_{liquid}}{\Delta P_{gas}}\right) = \left(\frac{L}{G}\right)^{1.8}\left(\frac{\rho_g}{\rho_l}\right)\left(\frac{\mu_l}{\mu_g}\right)^{0.2}$$

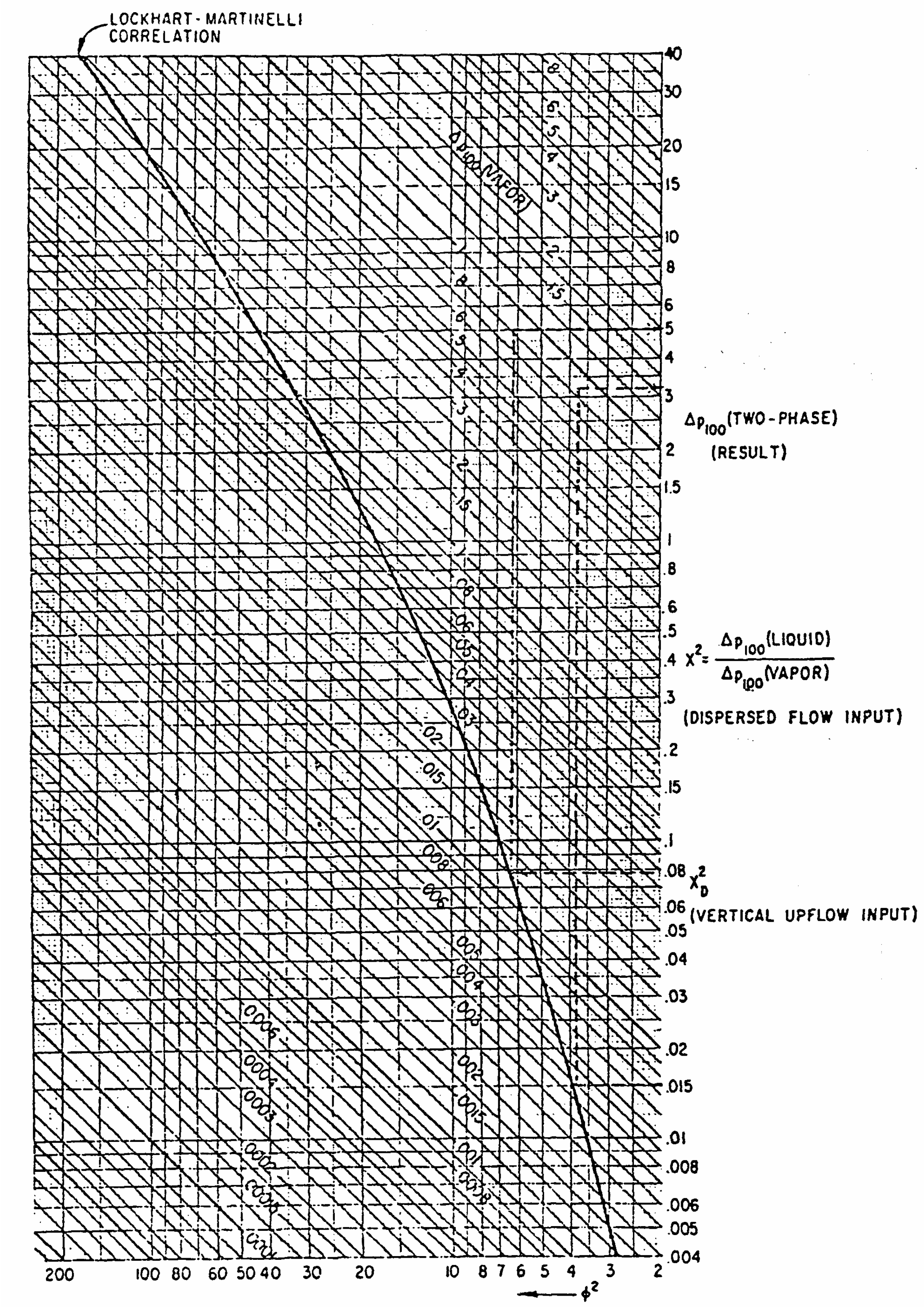
and for hydrocarbon-liquid vapour mixtures flowing at equilibrium

Equation 6-53

$$\left(\frac{\mu_l}{\mu_g}\right)^{0.2} \approx 1.6$$

$$x^2 = 1.6\left(\frac{L}{G}\right)^{1.8}\left(\frac{\rho_g}{\rho_l}\right)$$

Another simplification that can often be made is to calculate the term $\frac{G}{\lambda}$ and if it is greater than 80,000 then the flow is dispersed (spray) and figure 6.13 can be used to find the two phase pressure drop. Figures 6.19 and 6.20 give a simple way of finding the two phase pressure drop for annular and bubble flow respectively. The method is the same as for dispersed flow. That is, find *x*, enter the nomograph against the appropriate line, go up to the appropriate ΔP for the vapour and read off the $\Delta P_{two\ phase}$.



Two-phase flow unit losses for dispersed flow, vertical upflow (all flow regions), 2½-in. and smaller pipes (all flow regions).

Figure 6.13: Two phase flow unit losses for dispersed flow

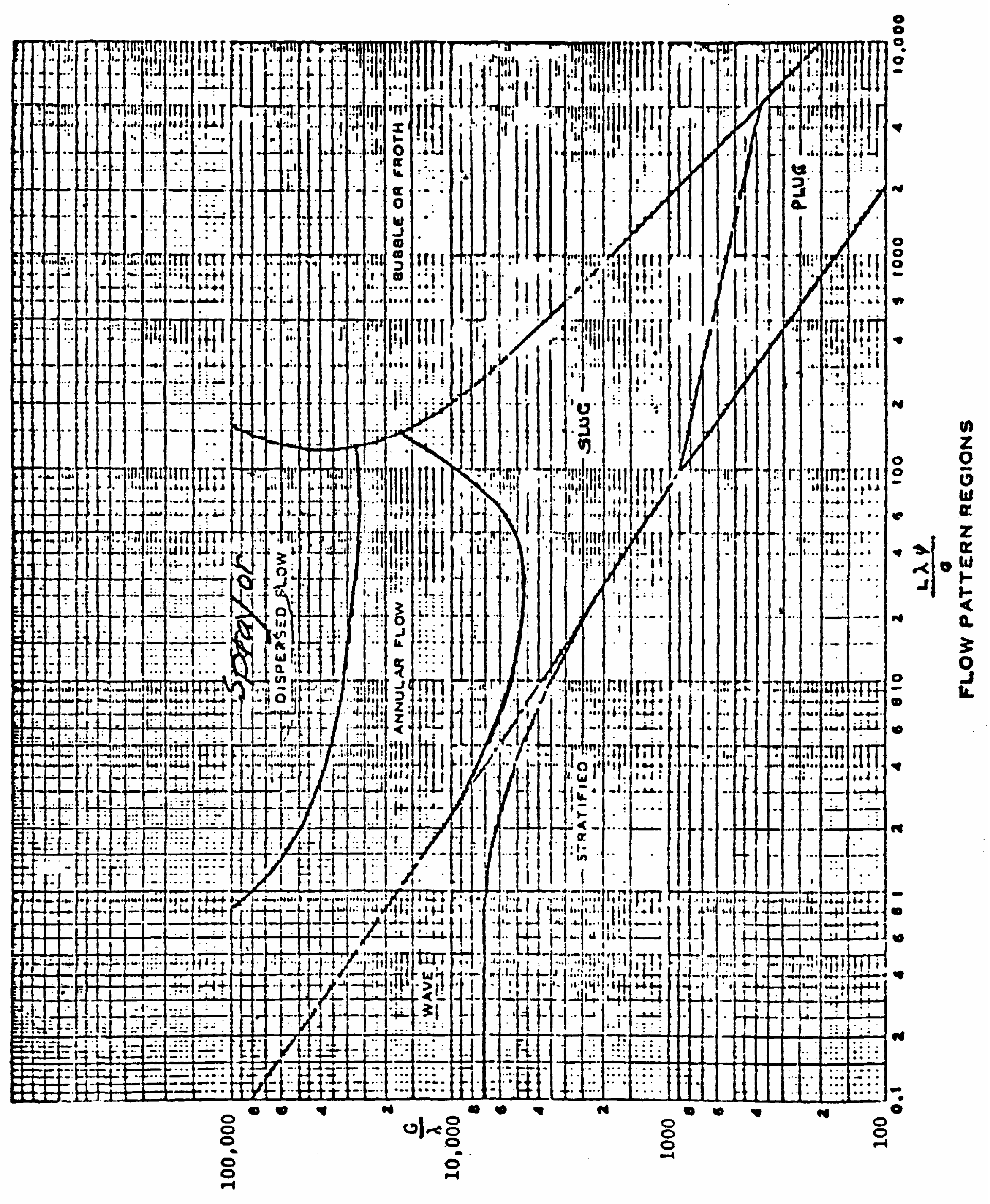
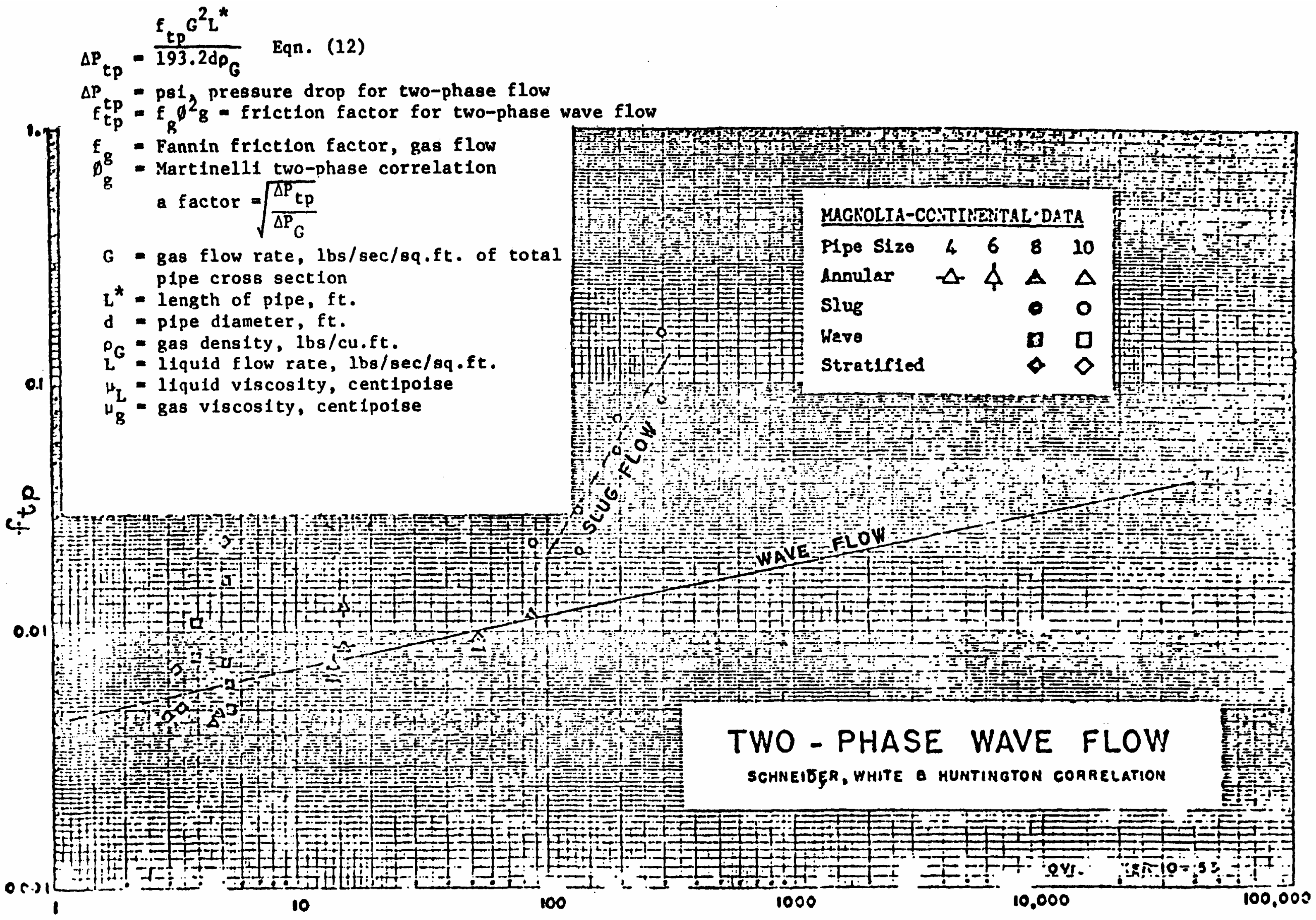


Figure 6.14: Flow Pattern Regions



$$\Delta P_{tp} = \frac{f_{tp} G^2 L^*}{193.2 d \rho_G} \quad \text{Eqn. (12)}$$

ΔP_{tp} = psi, pressure drop for two-phase flow
f_{tp} = $f_g \phi^2{}_g$ = friction factor for two-phase wave flow
f_g = Fannin friction factor, gas flow
ϕ_g = Martinelli two-phase correlation
a factor = $\sqrt{\frac{\Delta P_{tp}}{\Delta P_G}}$

G = gas flow rate, lbs/sec/sq.ft. of total pipe cross section
L^* = length of pipe, ft.
d = pipe diameter, ft.
ρ_G = gas density, lbs/cu.ft.
L = liquid flow rate, lbs/sec/sq.ft.
μ_L = liquid viscosity, centipoise
μ_g = gas viscosity, centipoise

MAGNOLIA-CONTINENTAL·DATA				
Pipe Size	4	6	8	10
Annular	-△-	△	▲	△
Slug			●	○
Wave			▣	□
Stratified			◆	◇

Figure 6.15: Two-Phase Wave Flow

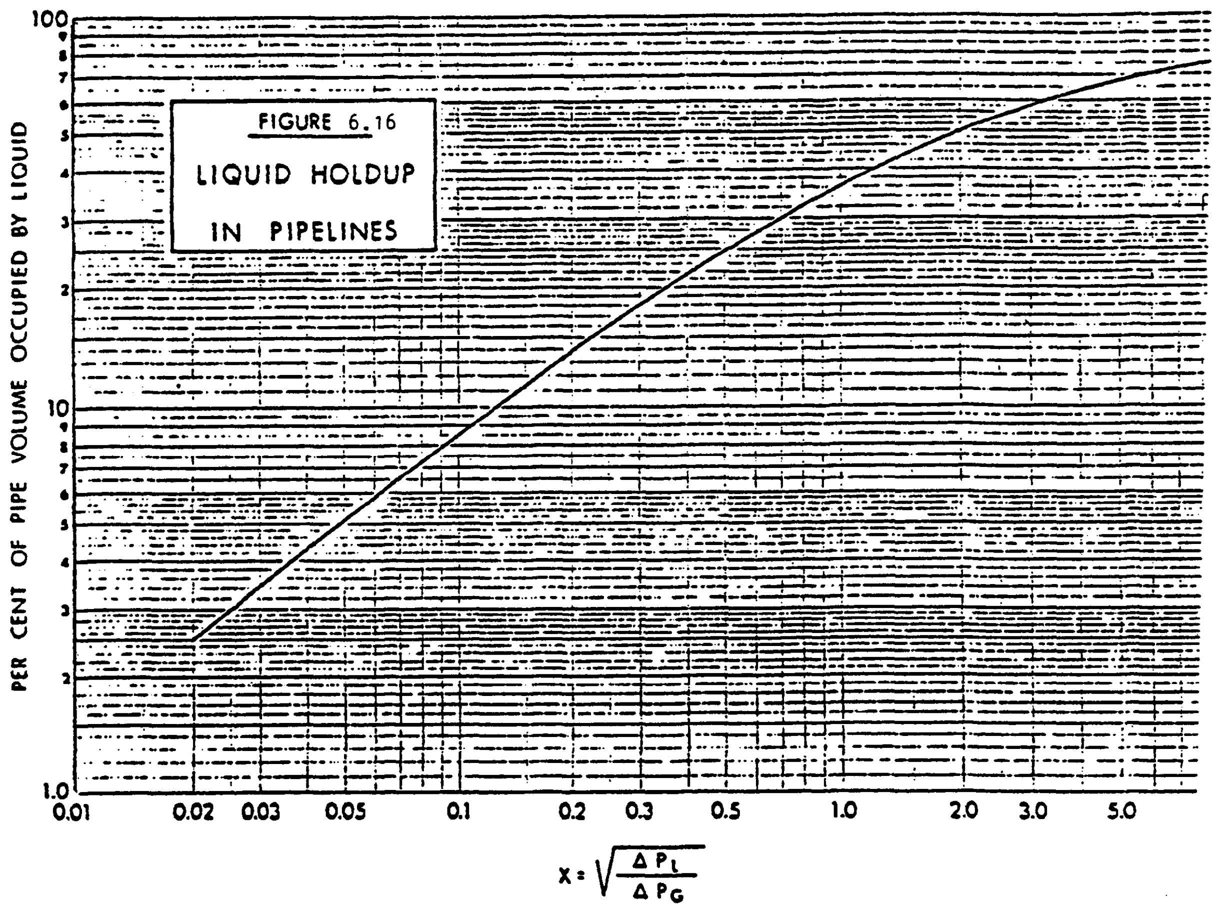


Figure 6.16: Liquid Holdup in Pipelines

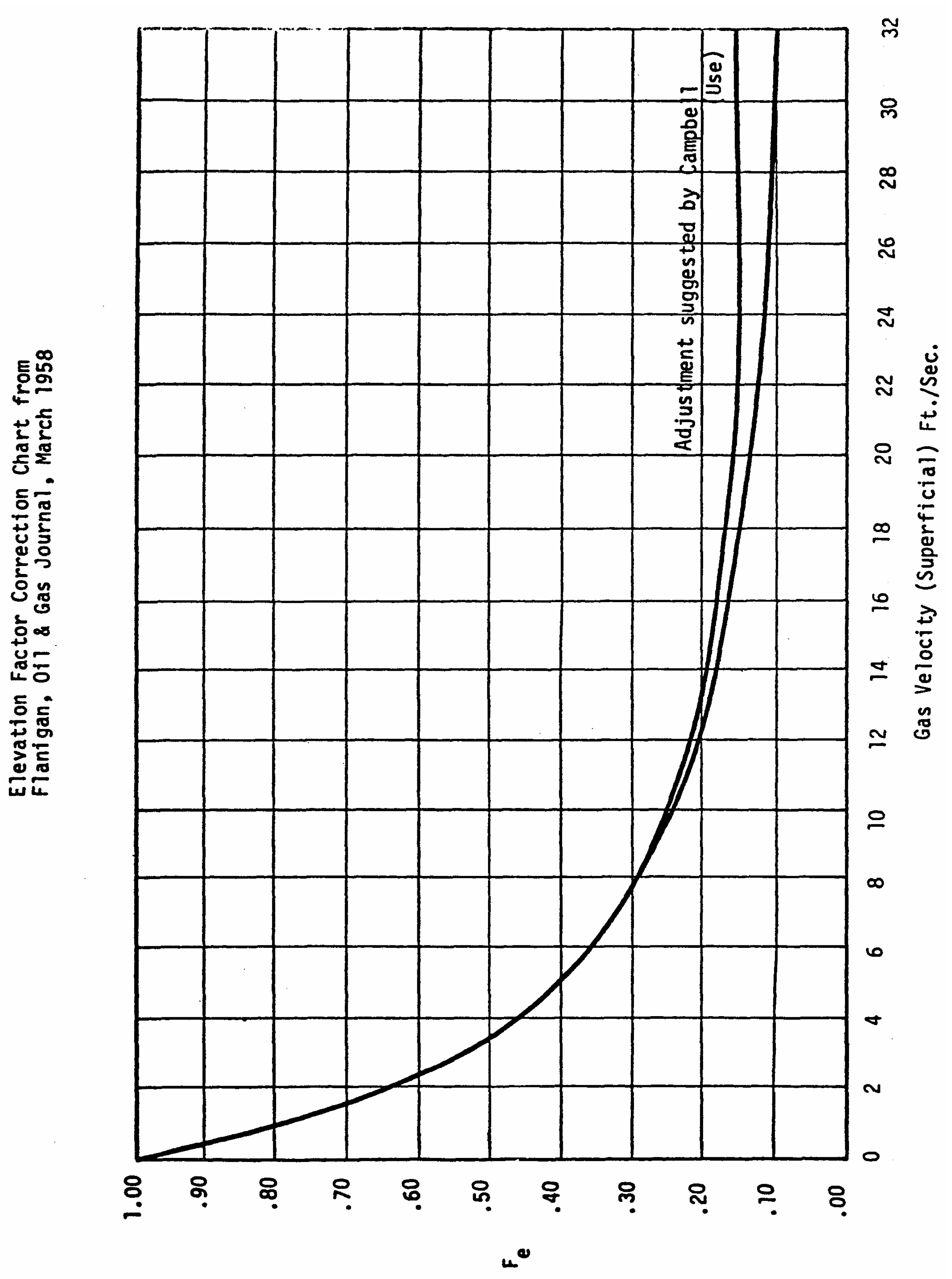


Figure 6.17: Elevation Factor Correction Chart from Flanigan, Oil & Gas Journal, March 1958

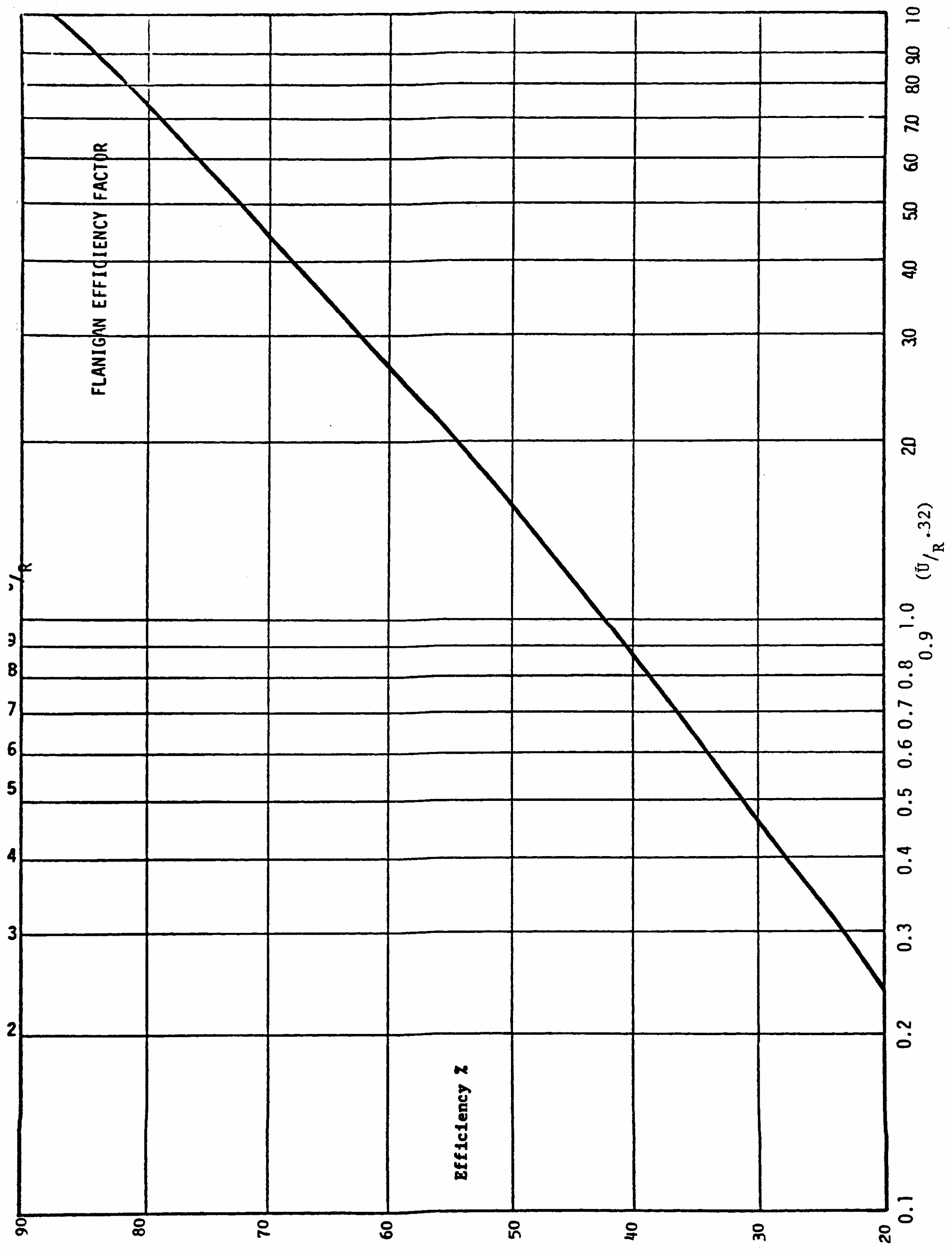
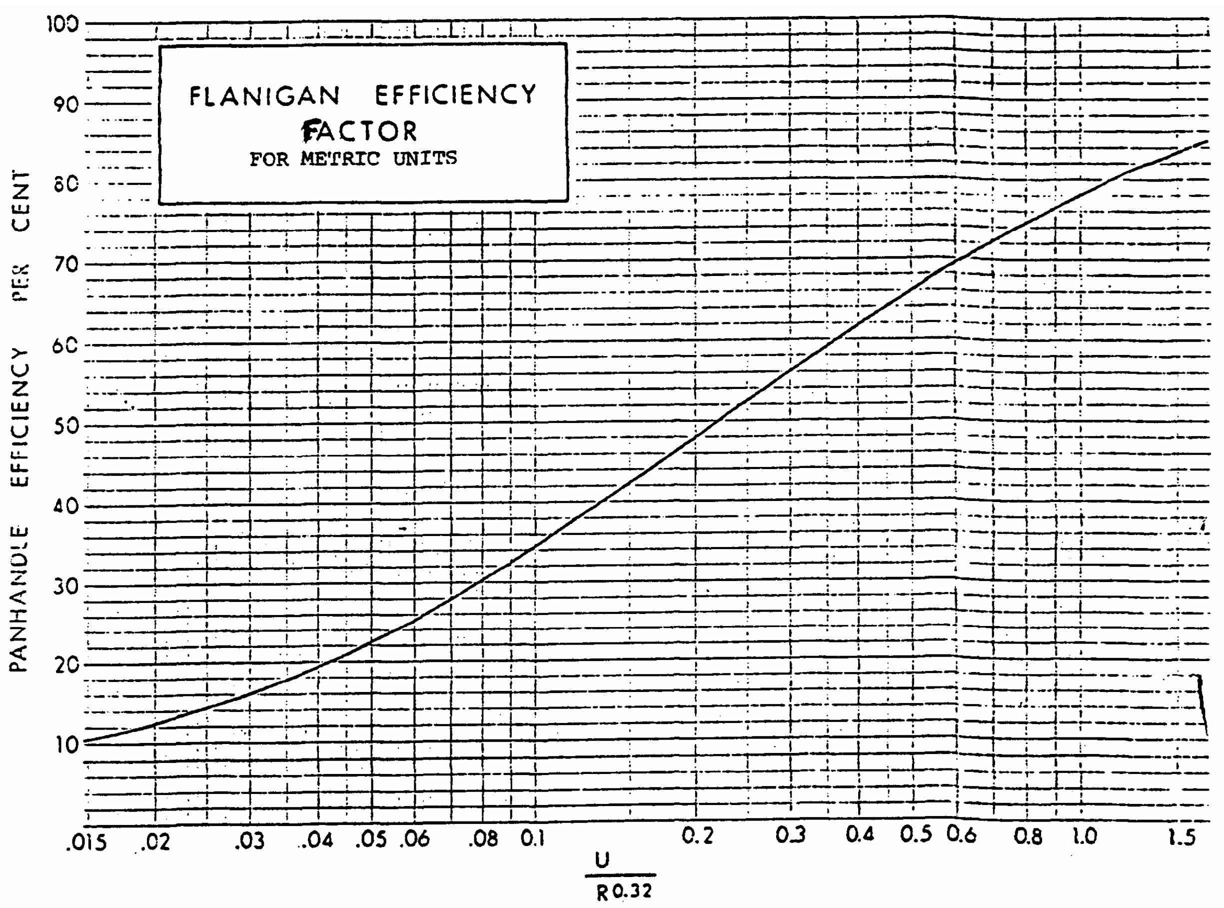


Figure 6.18: Flanigan Efficiency Factor

Flanigan Efficiency Factor for Metric Units



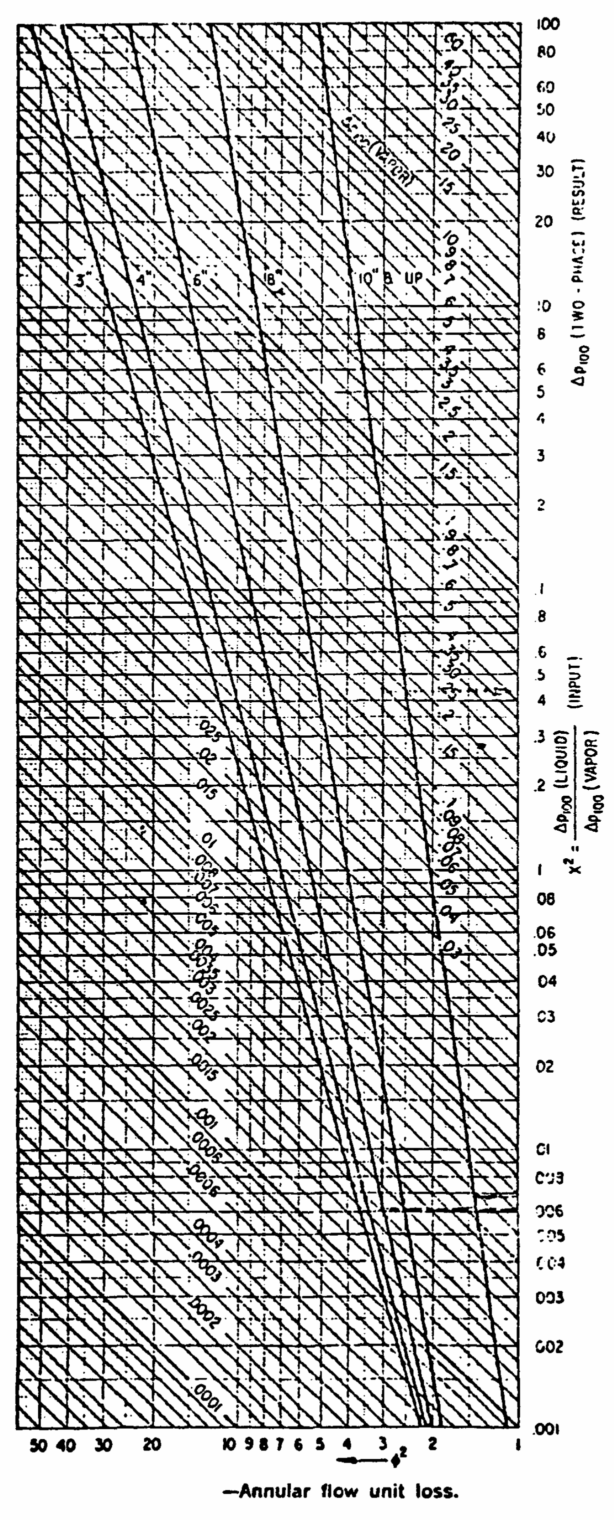


Figure 6.19: Annular Flow Unit Loss

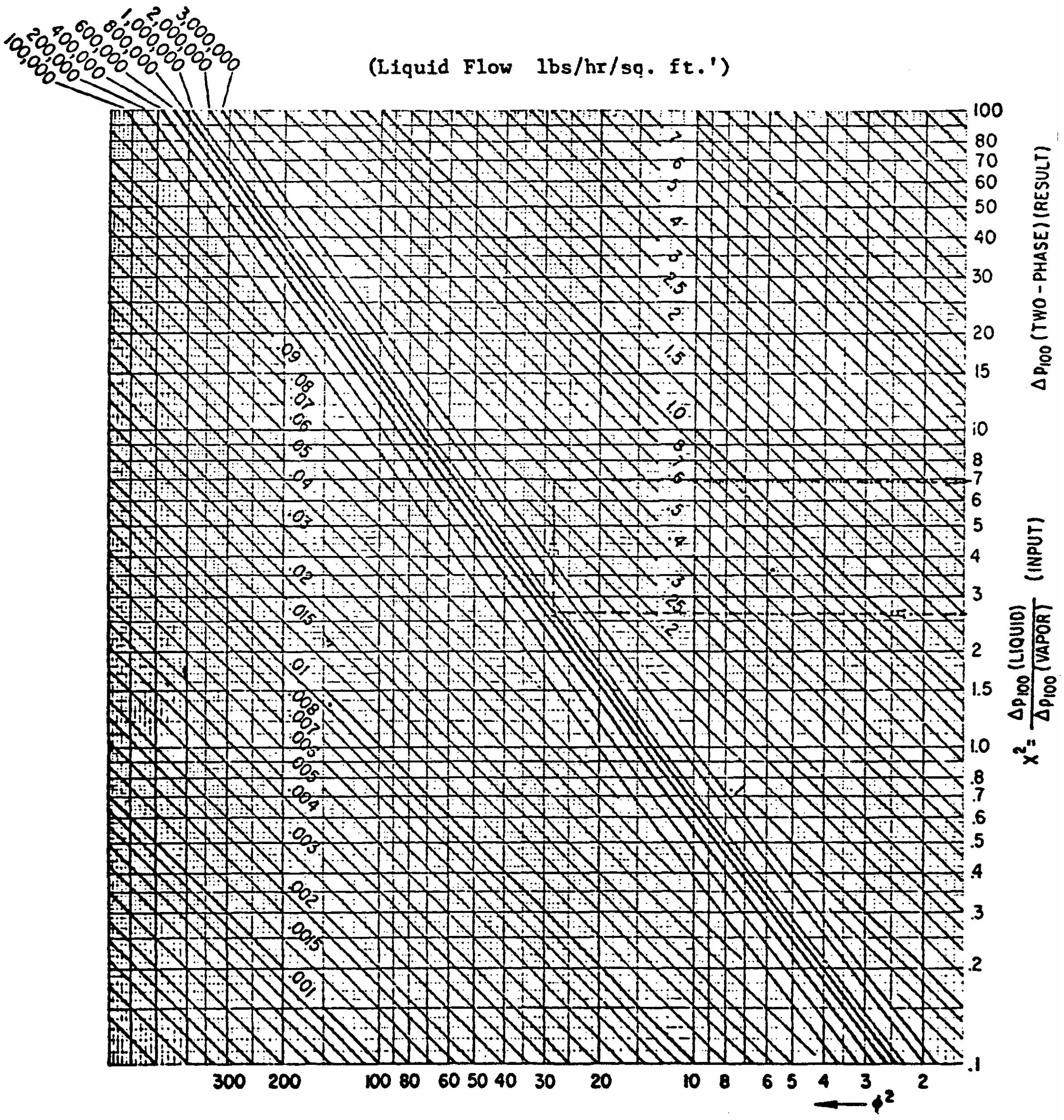


Figure 6.20: Bubble Flow Unit Loss

6.5.4 Liquid Holdup

Before we consider pipeline design, we should mention liquid holdup. The percent volume of pipe occupied by liquid is correlated by the factor x. We can have up to 80% by volume liquid. Figure 6.16 shows this data. This figure also can be used to illustrate the instability of two phase lines as a slight change in x can cause a considerable volume of liquid to come out of a line. For example, if the factor x changes from 0.8 to 1.0, the amount of liquid that will drop out is 5% of the total volume of the gathering system, which can be quite substantial. This explains the slugging that often occurs when increases in flows to a plant are required.

6.5.5 Pressure Drop Due to Elevation Change

In two phase flow liquid can accumulate in valleys, therefore it is necessary to allow for this in calculating the two phase pressure drop. This is done by the formula:

Equation 6-54

$$\Delta P_H = \frac{\sum h F_e \rho_L}{144}$$

where:

$\sum h$ = height of the hills which the line covers

F_e = elevation factor

ρ_L = liquid density

Note: F_e is obtained from data developed by Flanigan as a function of gas velocity and given in Figure 6.17.

6.5.6 Method of Flanigan[5] for Two Phase

This is quite a simple method for calculating ΔP_{TP}. It was developed for natural gas and condensate systems and probably is not applicable to other systems because physical properties of fluid are not taken into account. The method consists of finding a new efficiency factor "E" for the Panhandle formula. "E" is a function of the liquid content and the gas velocity.

6.5.6.1 The Flanigan Procedure

a) Find superficial gas velocity (velocity with no liquid present) "U"

b) Find "R", the bbls of liquid per MMSCF of gas

c) Calculate $\frac{U}{R^{0.32}}$

d) Read off pipeline efficiency from Figure 6.18

e) Calculate pressure drop from the Panhandle formula, inserting proper pipeline efficiency.

Note: GE Time Sharing has this as a program. It is called *FLANIS*.

6.5.7 Method of Gregory, Mandhane and Aziz[10]

Recently Gregory and Aziz[13], co-workers at The University of Calgary, developed a more sophisticated method for finding the pressure drop in two phase flow situations. They developed a slightly different flow diagram which is shown as Figure 6.21. This plots the superficial liquid velocity versus the superficial gas velocity. The various types of flow to be expected are shown on the diagram. Then after the type of flow is determined, a correlation for calculating the liquid holdup and pressure is selected according to the next table.

Table 6.7: Suggested Methods for Pressure Drop and Hold Up Calculations

Flow Regime	Holdup Prediction Method	Pressure Drop Prediction Method
Bubble, Elongated Bubble	Hughmark	Chenoweth and Martin
Stratified	Agrawal, Gregory and Govier	Agrawal, Gregory, and Govier
Wave	Chawla	Dukler, Wicks, and Cleveland
Annular, Annular Mist	Lockhart and Martinelli	Chenoweth and Martin
Dispersed	Beggs and Brill	Modified Lockhart and Martinelli

Note: Computer programs for each of the available at the University of Calgary.

In particular, their method is as follows:

1. For the given transportation problem, the superficial gas and liquid velocities, V_{SG} and V_{SL} respectively, are calculated for the conditions existing at the inlet of the pipeline.
2. Using Figure 6.21 and the values of V_{SG} and V_{SL} calculated above, the expected flow pattern is determined.
3. Knowing the predicted flow pattern, one then selects the particular methods recommended for predicting the liquid holdup, E_L, and the friction pressure drop, ΔP_f, from the table above.
4. The friction pressure drop, ΔP_f, and liquid holdup, E_L, are calculated for an increment of pipe length using the methods selected above. The total pressure drop over the increment of pipe length is then determined from the relation,

Equation 6-55

$$(\Delta P)_{increment} = \Delta P_f + (\Delta Z^+)\rho_M$$

where

Equation 6-56

$$\rho_M = \rho_L \, E_L + \rho_G (1 - E_L)$$

and ΔZ^+ is the change in elevation for which the flow is uphill. ΔZ^+ is zero for horizontal or downhill flow.

E_L is calculated from a holdup prediction method.

5. The procedure is then repeated for a new increment of pipe length, using the conditions at the downstream end of the previous increment as the basis of the calculation of new values of V_{SG} and V_{SL}.

In practice, a rather involved computer program is required to properly follow this procedure. Determining the superficial velocities of the gas and liquid generally requires a phase behavior calculation; provision for this must be built into the program. As the conditions change along the pipeline, some provision must be made to account for changes in the physical properties of the gas and liquid phases. Since the amount of gas flowing in the pipeline generally increases with decreasing pressure, an iterative calculation is required over the incremental length to match the downstream pressure to the flowing phase volumes. This can be further complicated by the existence of a temperature gradient in the direction of flow. The pipeline profile must be available as input data; changes in the slope of the pipeline at irregular intervals require that a variable length increment be possible. This is also the case where the flow is predicted to pass through a flow pattern transition. For completeness, Equation (55) should also be modified to include pressure loss due to kinetic energy effects.

In short, the proposed design strategy is not well suited to hand calculations. However, in view of the general accessability of computers, this is not believed to be a serious limitation.

Example Problem 6.2

Determine the size of a gas gathering line to handle 60 MMSCFD of a gas with an expected liquid content of 12 BBLs per MMSCF. The length of the line is 10.0 miles and the sum of the elevation difference is 500 ft. The gas is to be delivered to a processing plant at 950 psig. The maximum delivery pressure at the wellsite is 1200 psig. The average temperature in the pipeline is 70°F.

Some of the properties of the gas are:

SG = 0.65

Z at average conditions = 0.800

Actual density at average conditions = 7.100 lbs/cu.ft.

Some of the properties of the liquid are:

Density = 44.0 lbs/cu.ft.

Solution

Pressure drop available for flow = 250 psi

Let us use the method of Flanigan. Assume 8 in. diameter pipe. Calculate U, superficial gas velocity, via Flanigan Formula.

where:

$$U = \frac{31{,}194\,Z\,Q}{Pd^2} \text{ in ft/sec}$$

Q = Flow MMSCFD

P = Press psia

d = diameter inches

Z = compressibility factor

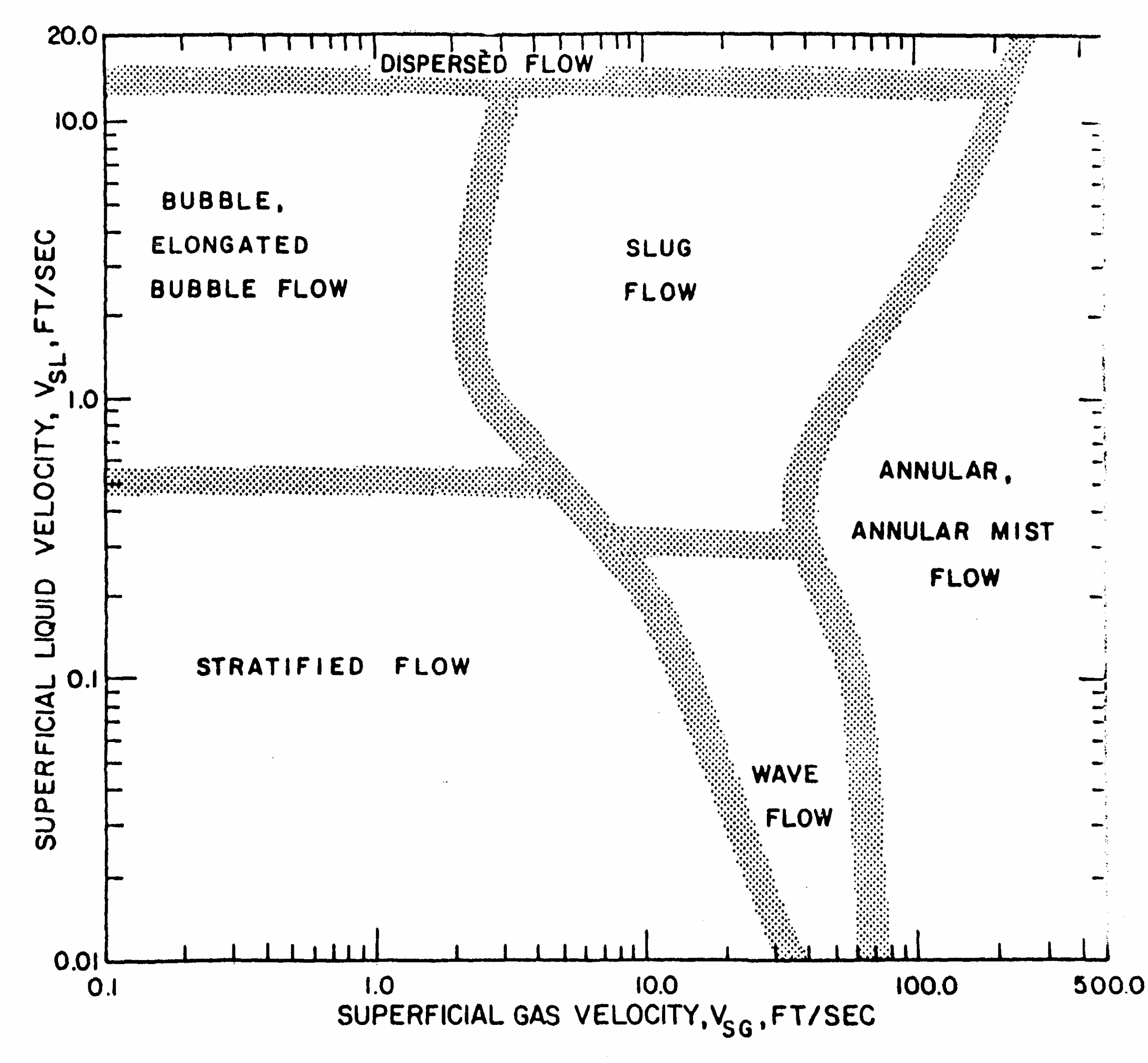


Figure 6.21: Two Phase Flow Types

$$U = \frac{31194(60)(0.800)}{(8)^2(1100)} = 21.3\ {}^{ft}\!/_{\sec}$$

From chart, $F_e = 0.12$

Pressure drop due to elevation difference

$$\Delta P_H = \frac{\rho_L F_e \sum h}{144} = \frac{44(0.12)(500)}{144} = 18.3\,psi$$

Next calculate the pressure drop due to friction:

Find

$$\frac{U}{R^{0.32}} = \frac{21.3}{(12)^{0.32}} = 9.7$$

From graph, line efficiency is equal to 86%.

We put this efficiency in the Panhandle Equation (Equation (40)).

$$Q = 435.87\,E\left(\frac{T_0}{P_0}\right)^{1.078}\left(\frac{P_1^2 - P_2^2}{L}\right)^{0.5394}\left(\frac{1}{T}\right)^{0.5394}\left(\frac{1}{G}\right)^{0.4606}\left(\frac{1}{Z}\right)^{0.5} d^{2.6182}$$

Solve for P$_2$

$$60\,x10^6 = 435.87(0.86)\left(\frac{520}{14.65}\right)^{1.078}\left(\frac{1215^2 - P_2^2}{L}\right)^{0.5394}\left(\frac{1}{530}\right)^{0.5394}\left(\frac{1}{0.65}\right)^{0.4606}\left(\frac{1}{0.8}\right)^{0.5} 8^{2.6182}$$

P$_2$ = 1020

The total pressure drop is 18.3 + 195 = 213 psi. This is probably okay for size but let us try a 10 in. diameter line. The superficial gas velocity is U.

$$U = \frac{31194(60)(0.80)}{(10)^2(1100)} = 13.6\ ft/\sec$$

F$_e$ from chart = 0.18

$$\Delta P_H = \frac{44(0.18)(500)}{144} = 27.5\ psi$$

Note how this rises as diameter increases, the pressure drops for hills, increases as velocity is slowed down. Find pressure drop due to friction.

$$\frac{U}{R^{0.32}} = \frac{13.6}{2.17} = 6.25$$

From the graph the line efficiency is equal to 77%. Now put this efficiency into the. Panhandle Equation and solve for P$_2$:

$$60\,x10^6 = 435.87(0.77)\left(\frac{520}{14.65}\right)^{1.0781}\left(\frac{1215^2 - P_2^2}{10}\right)^{0.5394}\left(\frac{1}{530}\right)^{0.5394}\left(\frac{1}{0.65}\right)^{0.4606}\left(\frac{1}{0.80}\right)^{0.5} 10^{2.6182}$$

P$_2$ = 1138 psi

The total pressure drop is 27.4 + 77 = 104

Unless there was a method of continuing to keep the wellhead pressure up, it would probably be better to make the line 10" instead of 8" - although 8" would do.

This problem could also be solved by the Baker Method. The procedure is to find the type of flow, from the graph that correlates

$$\frac{G}{\lambda} \text{ vs. } \frac{L\lambda\Psi}{G}$$

then find the value of θ_{GTT} for the type of flow. The pressure drop due to friction is then found from the formula:

$$\Delta P_{two\ phase} = \phi_{GTT}^{2}\ \Delta P_G$$

The elevation pressure drop is found as previously illustrated. This is shown below.

Solution using the Method of Baker (Modified by Kern)

First find λ

$$\lambda = \left[\left(\frac{\rho_G}{0.075}\right)\left(\frac{\rho_L}{62.3}\right)\right]^{1/2} \quad = \quad \left[\left(\frac{7.10}{0.075}\right)\left(\frac{44}{62.3}\right)\right]^{1/2} \quad = 8.1$$

Find G assuming a 10" line

$$Gas\ Flow\left({}^{lb}\!/\!{}_{day}\right) = \frac{60\,x10^2}{384}(0.69)(29) = 2.96\,x10^6\ {}^{lb}\!/\!{}_{day}$$

$$G = \frac{2.96\,x10^6}{24\left(\frac{\pi}{4}\frac{10^2}{144}\right)} = 226000\ \frac{{}^{lb}\!/\!{}_{hr}}{sq.ft.}$$

$$\frac{G}{\lambda} = \frac{226000}{8.1} = 28000$$

Must find Ψ since $\frac{G}{\lambda}$ < 80,000, to find type of flow.

$$\Psi = \frac{73}{\chi}\left[u_L\left(\frac{62.3}{\rho_L}\right)^2\right]^{1/3}$$

$$\chi = 22\,dynes/cm; \quad u_L \ = 0.5$$

$$\Psi = \frac{73}{22}\left[0.5\left(\frac{62.3}{44}\right)^2\right]^{1/3} = 3.3$$

Also find L

$$L = \frac{12(60)(350)(0.7)(144)}{78.9(24)} = 13200$$

Find ordinate on Figure 6.14 $\frac{L\lambda\psi}{G}$

$$= \frac{13200}{226000}(8.1)(3.3) = 1.56$$

Type of flow from Figure 6.14 is annular. Find pressure drop for gas alone ΔP_{100} (from GPSA Data Book).

= 0.2 psi/100 ft.

Use Figure 6.19 for finding $\Delta P_{\text{two phase}}$

First find X

$$x^2 = \left(\frac{13200}{226000}\right)^{1.8}\left(\frac{7.10}{44}\right)(1.6) = (0.058)^{1.8}(0.16)(1.6) = 0.00152$$

From Figure 6.19

$$\phi^2 = \frac{\Delta P_{TP}}{\Delta P_G} = 1.2 \qquad \Delta P_{TP} = 0.2(1.2) = 0.24$$

$$\Delta P_{two\ phase} = 0.24\ {}^{psi}\!/_{100\ foot\ of\ pipe}$$

or read directly off of Figure 6.19.

Total drop exclusive of elevation change

$$= 0.24\frac{5280}{100}(10) = 127\ psi$$

which is relatively close to the Flanigan Method. i.e. total drop would be 27.4 + 127 = 154.4 psi.

6.6 Measurement of Fluids

Section 1 of the GPSA Data Book should be reviewed in connection with this section.

6.6.1 Units of Measurement

1. Gas - primarily as standard cubic feet per day at varying pressure, bases, but one temperature, 60°F. The pressure bases are:

   15.025 psia

   14.900 psia

   14.730 psia

   14.650 psia

   14.400 psia

   In metric units it is generally m^3/day at 15°C and 101.325 kPa

Liquids - normally Barrels Per Day for crude oil.

For LPG's - Imperial or U.S. Gallons per day.

For gasoline or other finished products -thousands of Imperial Gallons per Day.

For plant process streams, pumps, discharge, etc. - U.S. gpm. In metric units generally m^3/hr or m^3/day.

For accounting purposes, considerable interest is now being shown in mass measurement in lbs/hr or Kg/hr.

Steam - lbs/hr or Kg/hr.

6.6.2 Measuring Instruments

2. Orifice Meter Equations - The prime measuring instrument is the differential pressure meter, primarily the orifice plate. In this device a restriction is placed in the pipeline to induce a pressure drop as shown in Figure 6.22

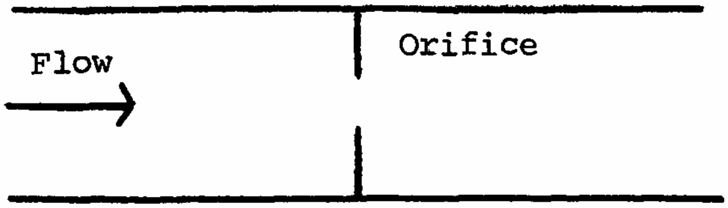


Figure 6.22: Orifice Plate Representation

The pressure drop that occurs is shown in the graph below

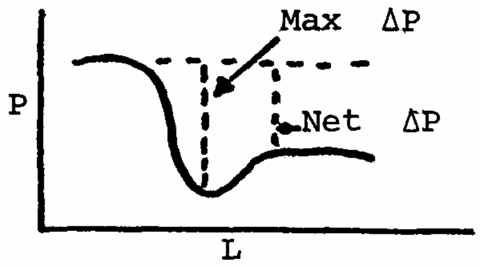


Figure 6.23: Pressure Drop in Orifice Plate

The general equation for an orifice meter is:

Equation 6-57

$$W = C_0\, A_0 \sqrt{\frac{2g_c\rho(\Delta P)}{1-\left(\frac{A_0}{A_1}\right)^2}}$$

where:

C_O = constant ≈ 0.62

A_O = area of orifice opening

ρ = density of fluid

gc = force of gravity

ΔP = pressure drop

A_1 = area of pipe

W = mass flow

This general equation has been changed into the following specific equation for gas by the American Gas Association in their report No. 3 reference. (Now ANSI/API 2500)

Equation 6-58

$$Q = C\sqrt{h_w\, P_f}$$

where:

Q = rate of flow in cu.ft./hr at the base conditions

h_w = measured pressure drop in inches of water

P_f = static pressure in psia (upstream value)

C = constant determined from the following data, all of which are available in the GPSA Data Book or AGA Report No. 3

$= (F_B)(F_{PB})(F_{TB})(Y)(F_{tf})(F_{pv})(F_R)(F_g)(F_L)$

These are:

F_B = Basic orifice factor which depends on where the differential pressure is measured and the ratios of orifice diameter to pipe diameter (β ratio).

F_{PB} = Pressure base factor

F_{TB} = Temperature base factor

Y = Expansion factor

F_g = Gravity of the gas

F_{tf} = Flowing temperature correction

F_{pv} = Super compressibility factor = $\frac{1}{\sqrt{Z}}$. The sour gas correction as developed by Wichert and Aziz as given in chapter 2, should be included in this factor if sour gas is being measured.

F_R = The Reynolds number factor

F_L = Correction for location other than 45° Latitude

For steam, the same equation, i.e. (58) is used by a different set of factors make up the constant C'. (See page 1-11 in the GPSA Data Book.)

For liquids, the static pressure is not a factor and the equation is

Equation 6-59

$$Q_h = C' \sqrt{h_w}$$

where:

Q_h = flow, US gallons per hour

C' = the orifice constant determined from a set of factors for liquids as given in the GPSA Data Book.

6.6.3 Two Phase Flow Measurement

E. Wichert of Canadian Fina has developed a reasonably accurate method. This method consists of measuring the two phase flow with a standard orifice using the gas properties and the measured differential, then correcting the measuring flow by means of the equation below:

Equation 6-60

$$Q_{TWE} = Q_{MP}\left(\frac{1 + R_{HL}\ E}{1 + R_{TL}\ S}\right)$$

where:

Q_{TWE} = Total hydrocarbon well effluent MMSCFD

Q_{MP} = The rate of flow obtained by using the properties of the gas phase with the multiphase meter readings for flow calculations.

R_H^L = liquid to gas ratio BBls/MMSCF

E = equivalent volume of liquid as a vapour at standard conditions MMSCF/BBl

$R_{TL} = R_{HL}+R_W$

R_W = water/gas ratio BBls/MMSCF

S = function of gas molar density (from Figure 6.24) at above 700 psia S = 0.0024 $\rho^{.2}$

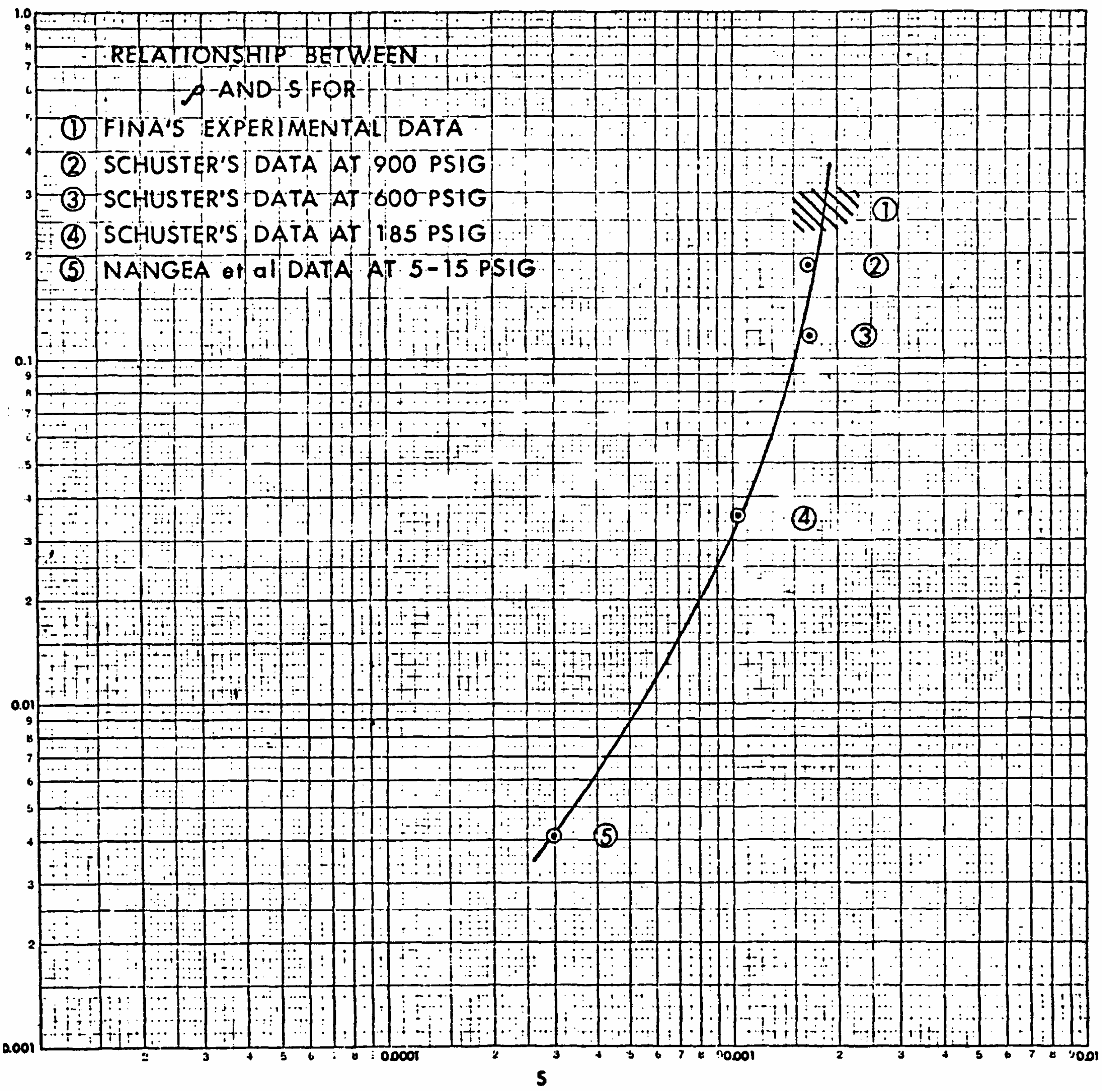


Figure 6.24: Function of Gas Molar Density

Orifice Meter Installations

The installation of orifices requires special care, particularly the presence of a close course of turbulence upstream has to be avoided. Some typical meter run installations are given in the GPSA Data Book (Page 1-8). These give the upstream and downstream requirements of straight pipe.

The measuring accuracy of an orifice meter is considered to be about 2%. Some companies claim 1% with extra long runs, no turbulent sections upstream, etc.

Venturi Meters

These operate on the same principle as an orifice (a differential pressure). However, the loss of pressure in the meter is much less. The coefficient of discharge is 0.92 to 0.98 compared to 0.62 with an orifice. As we know, it has a smoothly contoured throat rather than a sharp edge.

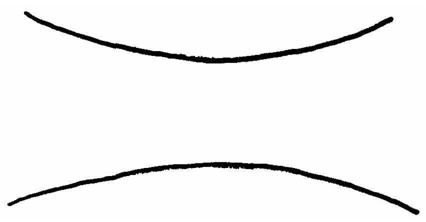


Figure 6.25: Venturi Meter

The Venturi is used primarily in large water lines, not gas lines. Use the general equation given previously with C_O - .92 to .98, .98 above 100,000 Re.

Flow Tube

Figure 6.26: Flow Tube

This is smaller than Venturi, measures small differences in pressure. It is sometimes used in large gas lines.

Area Meters

These are taper tubes with plugs in some. The pressure drop remains the same but area is allowed to vary by the motion of the meter.

Volume Meters

For low pressure, volume meters, such as the wet test meter, are used. The meter, half filled with liquid, has rotating blades which measure flow.

Turbine Meters

In this velocity of rotation is proportional to flow rate. API Standard 2534 covers turbine meters.

Liquid Meters

All the above referred to meters can be and are used for liquids. However, often positive displacement meters such as rotating lobes, wobbling discs, pistons, etc., are used for measuring liquids, particularly for finished products.

Both turbine and positive displacement liquid meters require periodic prooving to check counter registration versus gross volume. There are several types of liquid meter provers. These are discussed in the GPSA Data Book. Another instrument that is coming into prominence is the vortex meter which measures the number of vortices produced.

There is now a move to mass flow measurement. This is discussed on Pages 1-12 and 1-13 of the GPSA Metric Data Book.

A very good summary of measurement calculation is shown on Fig. 3-2 and Fig. 3-3 on the new English GPSA Data Book which are reproduced here.

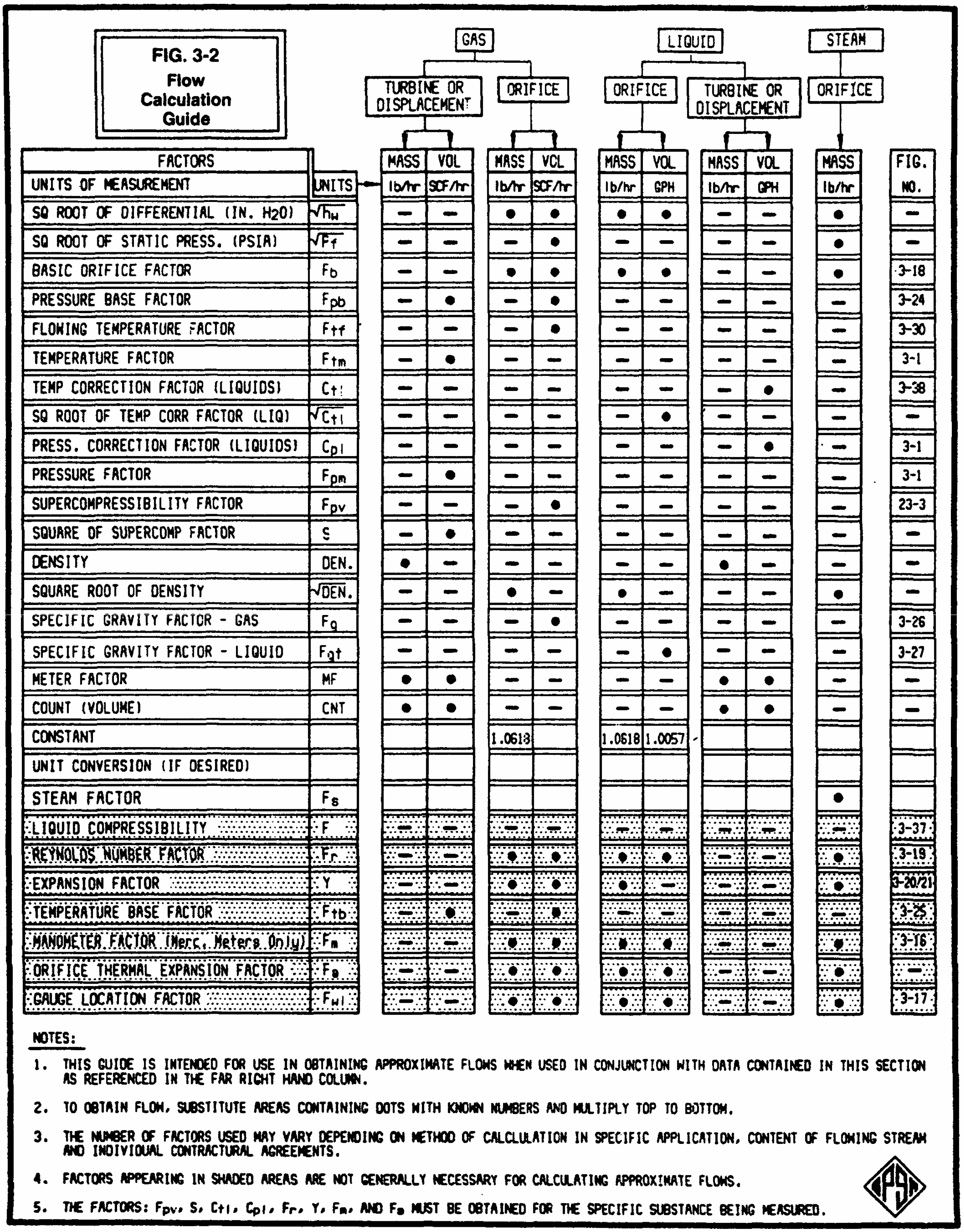


FIG. 3-2
Flow Calculation Guide

FACTORS		GAS				LIQUID				STEAM	
		TURBINE OR DISPLACEMENT		ORIFICE		ORIFICE		TURBINE OR DISPLACEMENT		ORIFICE	
		MASS	VOL	MASS	VCL	MASS	VOL	MASS	VOL	MASS	FIG. NO.
UNITS OF MEASUREMENT	UNITS	lb/hr	SCF/hr	lb/hr	SCF/hr	lb/hr	GPH	lb/hr	GPH	lb/hr	
SQ ROOT OF DIFFERENTIAL (IN. H_2O)	$\sqrt{h_w}$	—	—	●	●	●	●	—	—	●	—
SQ ROOT OF STATIC PRESS. (PSIA)	$\sqrt{F_f}$	—	—	—	●	—	—	—	—	●	—
BASIC ORIFICE FACTOR	F_b	—	—	●	●	●	●	—	—	●	3-18
PRESSURE BASE FACTOR	F_{pb}	—	●	—	●	—	—	—	—	—	3-24
FLOWING TEMPERATURE FACTOR	F_{tf}	—	—	—	●	—	—	—	—	—	3-30
TEMPERATURE FACTOR	F_{tm}	—	●	—	—	—	—	—	—	—	3-1
TEMP CORRECTION FACTOR (LIQUIDS)	C_{tl}	—	—	—	—	—	—	—	●	—	3-38
SQ ROOT OF TEMP CORR FACTOR (LIQ)	$\sqrt{C_{tl}}$	—	—	—	—	—	●	—	—	—	—
PRESS. CORRECTION FACTOR (LIQUIDS)	C_{pl}	—	—	—	—	—	—	—	●	—	3-1
PRESSURE FACTOR	F_{pm}	—	●	—	—	—	—	—	—	—	3-1
SUPERCOMPRESSIBILITY FACTOR	F_{pv}	—	—	—	●	—	—	—	—	—	23-3
SQUARE OF SUPERCOMP FACTOR	S	—	●	—	—	—	—	—	—	—	—
DENSITY	DEN.	●	—	—	—	—	—	●	—	—	—
SQUARE ROOT OF DENSITY	√DEN.	—	—	●	—	●	—	—	—	●	—
SPECIFIC GRAVITY FACTOR - GAS	F_g	—	—	—	●	—	—	—	—	—	3-26
SPECIFIC GRAVITY FACTOR - LIQUID	F_{gt}	—	—	—	—	—	●	—	—	—	3-27
METER FACTOR	MF	●	●	—	—	—	—	●	●	—	—
COUNT (VOLUME)	CNT	●	●	—	—	—	—	●	●	—	—
CONSTANT				1.0618		1.0618	1.0057				
UNIT CONVERSION (IF DESIRED)											
STEAM FACTOR	F_s									●	
LIQUID COMPRESSIBILITY	F	—	—	—	—	—	—	—	—	—	3-37
REYNOLDS NUMBER FACTOR	F_r	—	—	●	●	●	●	—	—	●	3-19
EXPANSION FACTOR	Y	—	—	●	●	●	—	—	—	●	3-20/21
TEMPERATURE BASE FACTOR	F_{tb}	—	●	—	●	—	—	—	—	—	3-25
MANOMETER FACTOR (Merc. Meters Only)	F_m	—	—	●	●	●	●	—	—	●	3-16
ORIFICE THERMAL EXPANSION FACTOR	F_a	—	—	●	●	●	●	—	—	●	—
GAUGE LOCATION FACTOR	F_{wl}	—	—	●	●	●	●	—	—	●	3-17

NOTES:

1. THIS GUIDE IS INTENDED FOR USE IN OBTAINING APPROXIMATE FLOWS WHEN USED IN CONJUNCTION WITH DATA CONTAINED IN THIS SECTION AS REFERENCED IN THE FAR RIGHT HAND COLUMN.
2. TO OBTAIN FLOW, SUBSTITUTE AREAS CONTAINING DOTS WITH KNOWN NUMBERS AND MULTIPLY TOP TO BOTTOM.
3. THE NUMBER OF FACTORS USED MAY VARY DEPENDING ON METHOD OF CALCLULATION IN SPECIFIC APPLICATION, CONTENT OF FLOWING STREAM AND INDIVIDUAL CONTRACTURAL AGREEMENTS.
4. FACTORS APPEARING IN SHADED AREAS ARE NOT GENERALLY NECESSARY FOR CALCULATING APPROXIMATE FLOWS.
5. THE FACTORS: F_{pv}, S, C_{tl}, C_{pl}, F_r, Y, F_m, AND F_a MUST BE OBTAINED FOR THE SPECIFIC SUBSTANCE BEING MEASURED.

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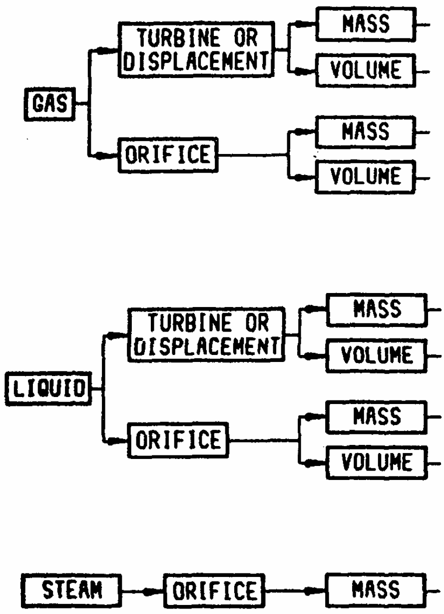
FIG. 3-3
Flow Calculation Guide Equations



$\text{lb/hr} = DEN \bullet MF \bullet CNT$ EQ. 3-1

$\text{SCF/hr} = F_{pb} \bullet F_{tm} \bullet F_{pm} \bullet S \bullet MF \bullet CNT \bullet F_{tb}$ EQ. 3-2

$\text{lb/hr} = \sqrt{h_w} \bullet F_b \bullet \sqrt{DEN} \bullet 1.0618 \bullet F_r \bullet Y \bullet F_m \bullet F_a \bullet F_{wl}$ EQ. 3-3

$\text{SCF/hr} = \sqrt{h_w} \bullet \sqrt{P_f} \bullet F_b \bullet F_{pb} \bullet F_{tf} \bullet F_{pv} \bullet F_g \bullet F_r \bullet Y \bullet F_{tb} \bullet F_m \bullet F_a \bullet F_{wl}$ EQ. 3-4

$\text{lb/hr} = DEN \bullet MF \bullet CNT$ EQ. 3-1

$\text{GPH} = C_{tl} \bullet C_{pl} \bullet MF \bullet CNT$ EQ. 3-5

$\text{lb/hr} = \sqrt{h_w} \bullet F_b \bullet \sqrt{DEN} \bullet 1.0618 \bullet F_r \bullet Y \bullet F_m \bullet F_a \bullet F_{wl}$ EQ. 3-3

$\text{GPH} = \sqrt{h_w} \bullet F_b \bullet \sqrt{C_{tl}} \bullet F_g \bullet 1.0057 \bullet F_r \bullet F_m \bullet F_a \bullet F_{wl}$ EQ. 3-6

$\text{lb/hr} = \sqrt{h_w} \bullet F_b \bullet F_s \bullet F_r \bullet Y \bullet F_a \bullet \sqrt{P_f}$ EQ. 3-3 S

Other Equations:

$Q = C'\sqrt{h_w \bullet P_f}$ EQ. 3-7

$C^1 = F_b \bullet F_{pb} \bullet F_{tf} \bullet F_{pv} \bullet F_g \bullet F_r \bullet Y \bullet F_{tb} \bullet F_m \bullet F_a \bullet F_{wl}$ EQ. 3-8

6.7 MOVING OF FLUIDS

The two main pieces of fluid moving equipment are pumps and compressors. We are not going to touch on all various types of pumps, such as centrifugal, turbine, reciprocating, gear, etc., or discuss the advantages or disadvantages of reciprocating or centrifugal compressors, or discuss the type of compressor to use. However, we would like to review some of the problems in selecting the proper pieces of equipment to do the job.

6.7.1 Specification of Pumps

There are several process items to be selected by an engineer specifying a pump.

These are:

1. Fluid being pumped.
2. Specific gravity of fluid at its operating temperature and 60°F.
3. Viscosity at operating temperature.
4. Operating temperature.
5. Capacity (use about 10% above process flow sheet for ordinary services and 25% for reflux services).
6. Head.
7. Net positive suction head available (NPSH).

The first five are obtained from flow diagrams or physical property tables. This leaves three classifications.

Capacity

For the capacity an allowance of 10% above material balance figures should be used.

Head

For determining the head, first make a sketch of the system as shown in the sketch accompanying the example problem. To find the pump head required, list pressure drop pump has to overcome, i.e.

1. Terminal pressure in tower - from process flow sheet.
2. Pressure drop in discharge piping – calculate.
3. Heat exchange pressure drop - 10 psi (normally, or actual value, if available).
4. Control valve & controller pressure - 10 psi (or take about 1/3 of total available system drop).
5. Determine the difference in elevation.
6. Add 5% over plus. This gives the head required.

NPSH

This determines whether a pump will cavitate or not.

The NPSH is found from the formula:

Equation 6-61

$$NPSH = P_1 - VP + H_1 - H_2 - F$$

where:

P_1 = actual pressure in suction drum

VP = vapour pressure of liquid being pumped

H_1 = minimum level in suction tank

H_2 = height of impeller eye above grade

F = friction loss in the suction line to the pump in feet

The reason that NPSH is so important is that it is a measure of cavitation or vapourization possibilities in a pump. Cavitation causes pits, etc. in pump impeller.

Refer to the article by A.H. Younger and J.L. Reuter , for further discussion on the calculation of heads and NPSH.

An example problem will illustrate this sizing of pumps.

Example Problem 6.3

Calculate the head and NPSH required for pumping 60 US gpm of mixed butanes from a feed tank that operates at 50 psig and 80°F into a fractionating tower that operates at 200 psig. The following sketch illustrates the system.

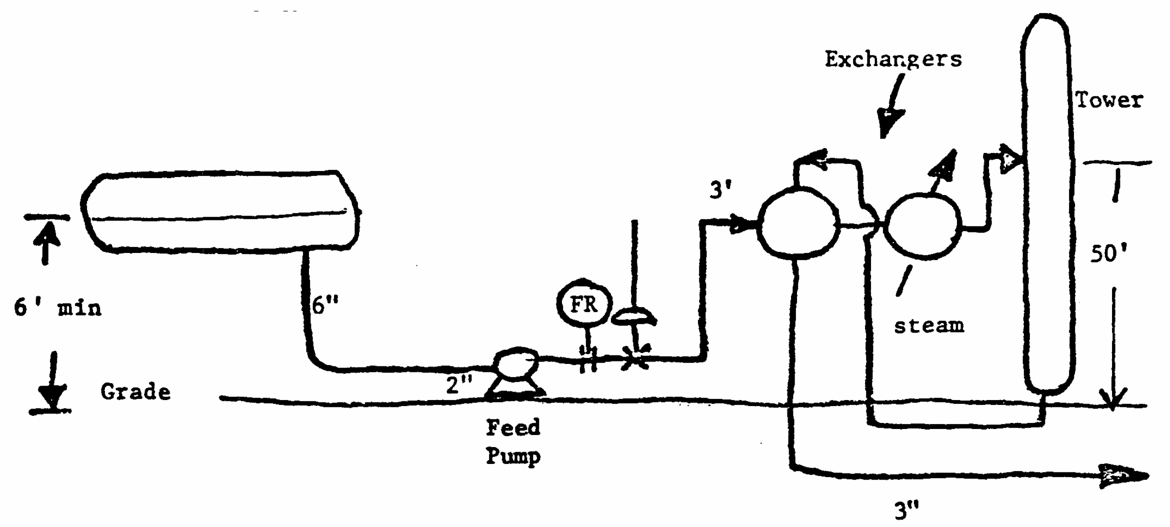


Figure 6.27: Mixed Butanes from a Feed Tank

Head Calculations	Head in Feet 1 psi = 4' for C_4
Terminal Pressure (200 psig)	
Suction Pressure (50 psig)	
Net Pressure Difference (150 psi)	600
Elevation Difference (50 - 2)	48
Control Valve (10 psi)	40
Heat Exchangers (.10 psi ea.)	80

Piping (400 equivalent feet)	48
Sub Total	816
Add 5% for safety factor	42
Total	858

NPSH Calculations

Use formula NPSH = (Pi - VP) + $H_1 - H_2$ - F)

	Feet
Pi (Suction pressure 50 psig)	200
VP (Vapour Pressure at suction temp 50 psig)	200
H_1	6
H_2	2
F (Assume 1 ft. unless it is higher)	1
	3

6.7.2 Compressor Specifying

In this case it is necessary to specify the following:

3. Gas to be compressed and its properties, i.e., mole weight and ratio of specific heat.

Equation 6-62

$$\frac{C_P}{C_V} = K$$

Gas temperature at suction end of compressor.

Gas pressure at suction end of compressor.

Flow in SCFM or SCFD, etc. use process flow sheet flow plus 5% to 10%.

Discharge pressure. Calculate in the same manner as for pumps. Specify discharge pressure with the following additional margin:

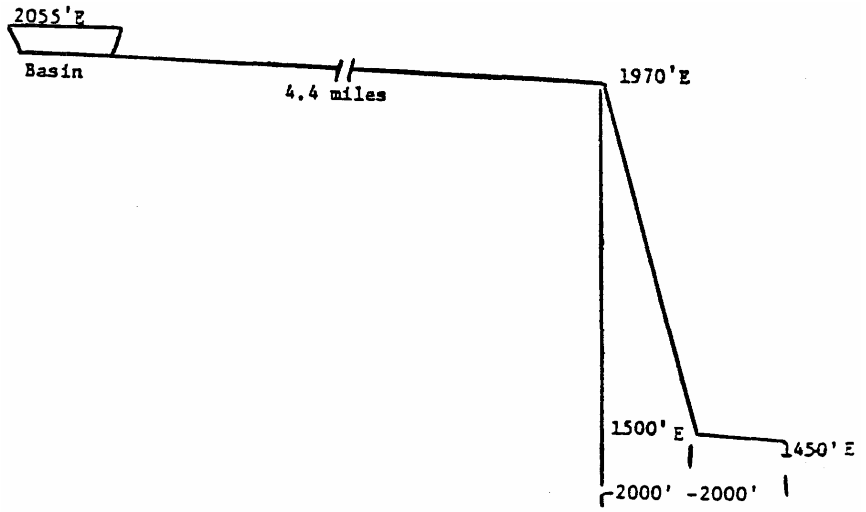
Comp. Patio	**Pressure Drop**
6 or less	3%
7 to 36	5%
over 36	10%

See example problem 1 in Section 10.

6.8 Example Problems

Example Problem 6.4

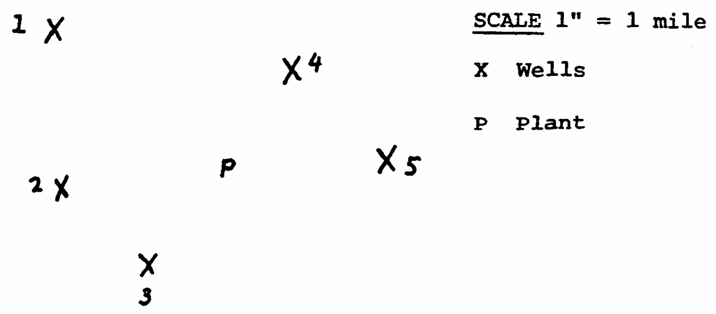
You are to size the pipeline to carry waste water fran a settling basin in a plant to a river. The design flow rate is 200 US gpm and the profile and length of line is as follows:



Note: Make the line the same size throughout.

Example Problem 6.5

You are to size a gathering system for the field shown in the sketch below. The plant is to receive the gas at a minimum pressure of 600 psia. The gas gravity is 0.65. The well deliverability pressure is 705 psia.



The wells have the following deliverability.

	MMSCFD
#1	8
#2	15
#3	20
#4	12
#5	30

The cost of installation of a pipeline is $6000/inch diameter mile.

Calculate the cost of your gathering system and show it on a sketch.

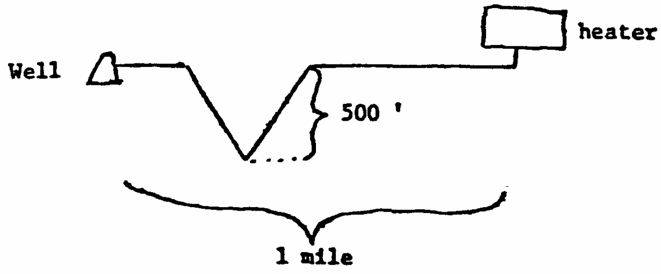
Assume that the reservoir has a water drive and the deliverability pressure will never decrease.

Example Problem 6.6

A large gas gathering line is pigged every day. This line goes through a river valley 1000 feet deep. Approximately how much greater is the pressure at the upstream side of the pig when the pig is in the bottom of the valley as compared to the pressure at the top of the valley on the downstream side of the valley? The line size is 20" (19.250" ID) and the flow is 140 MMSCFD. The gas contains 30 BBls per MMSCFD of liquid. The operating pressure is 1100 psig and the operating temperature is 70°F. The gas gravity is 0.70 and the liquid's density is 45 lbs/cu.ft.

Example Problem 6.7

Determine the line size for a gas gathering line delivering gas to a heater located as shown in the sketch.



Length of line from well to dehydration is 1 mile. The best line is one with the lowest pressure drop. The gas flow is 15 MMSCFD. At the wellhead pressure is 800 psi. It contains liquid of 50 BBls/MMSCF with a density of 40 lbs per cubic foot. The gas gravity is 0.7 and the Z factor is 0.9. Data on pressure drop for various line sizes are shown in the following table. Make your choices from these line sizes.

Size	ΔP Gas Only psi	ΔP Liquid Only psi
8"	10	1
6"	20	1.5
4"	60	4
3"	140	8

Example Problem 6.8

You are to specify the head required for pumping propane from storage bullets that operate in a plant in which the local temperature goes down to -20°F through a 8" pipeline approximately 12 miles long and into a salt storage cavern that has brine specific gravity 1.2 as the means that holds pressure in the cavern. The cavern is 2000 feet deep. Also in the 12 mile pipeline there is a section of 6" pipe that is used to cross a lake. It is 2 miles long.

Note: Express your answer in feet of head.

Also estimate the NPSH required for the pump if the pump suction is at 2 ft. above grade and the minimum liquid tank level is 10 ft. The suction line is only 20 ft long and is 12 inches in size. The flow in the lines is to be 40,000 BPD.

Example Problem 6.9

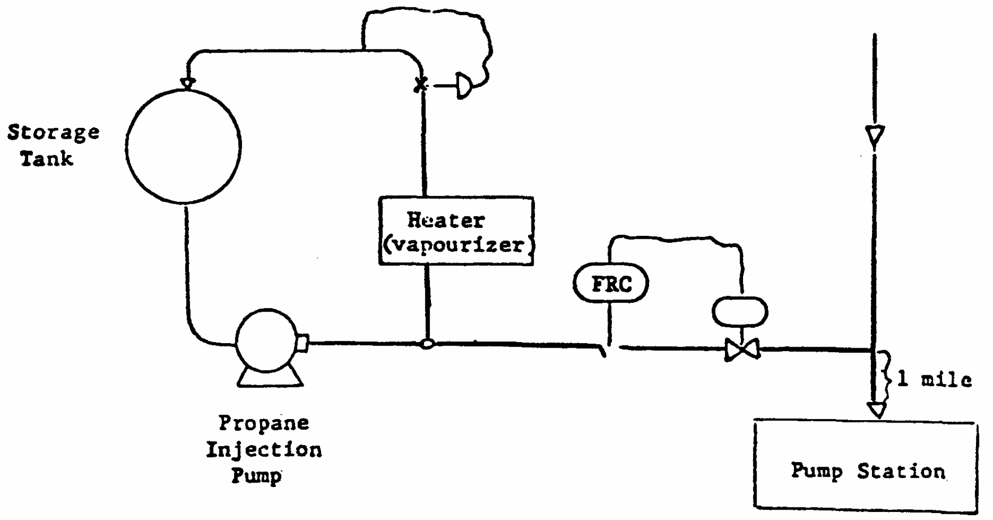
Propane is kept in a refrigerated storage vessel at +20°F which has 120,000 BBls capacity. It is being pumped out of this vessel into a pipeline at a rate of 200,000 BPD. The pipeline pump station is one mile farther down the line from the injection point. The pump station suction pressure is to be 25 psia above the vapour pressure of the propane at the maximum pipeline temperature.

A vapourizer is put in to keep the pressure on the when pumping is in progress.

a) Determine the heat duty required by the vapourizer.

b) Determine head and capacity of the propane pump in and US gpm.

The sketch below shows the proposed system.



- The maximum temperature in the pipeline at any time is 65°F.
- Assume pure propane for your calculations.
- Assume a 5 psi pressure drop across the FRC valve and orifice meter in propane injection line.
- Assume that the 100,000 barrels is moved at one time.

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2. R.J. Anderson and T.W.F. Russel, "Designing for Two Phase Flow", Parts I, II and III, chemical Engineering, Dec. 6, 1965, 139 to Jan. 3, 1966, P. 87.
3. M. Talwar, "Economic pipe diameter and fluid flow calculations", Oil & Gas Journal, March 12, 1984, Page 85.
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7.0 Mass Transfer

- The principles of mass transfer and a review of unit operations based on mass transfer, distillation, absorption and adsorption

7.1 Introduction

7.1.1 What is a Mass Transfer?

It is the movement of one or more compounds between phases. We are primarily interested in transfer between liquid and gas but we do encounter in natural gas processing the transfer of mass between two liquid phases which are immiscible. You can, of course, have mass transfer between miscible phases, particularly when there is a permeable or semipermeable membrane, i.e. gas diffusion, osmosis, etc. Also if there is no membrane present we have a form of mass transfer in thermal diffusion.

7.1.2 Types of Processes Considered

Mass transfer operations we wish to consider are:

- Gas - Liquid
  - ➢ Distillation of Fractionation
  - ➢ Absorption
  - ➢ Stripping
- Liquid-Liquid
  - ➢ Liquid-Liquid Extraction
- Gas - Solid
  - ➢ Adsorption
  - ➢ Desorption

7.1.3 Primary Concepts

There are three primary concepts in mass transfer. These are:

1. Stages and the Ideal Stages
2. Continuous Transfer
3. Batch Transfer

Stages and the Ideal Stages

If two insoluble phases come together so that the various components can distribute themselves between the phases and the phases are mechanically separated, then this operation is called a stage. If enough time is allowed for complete equilibrium to occur such that additional time will not change the composition, then an ideal stage has been reached.

Let us consider a distillation tray as shown.

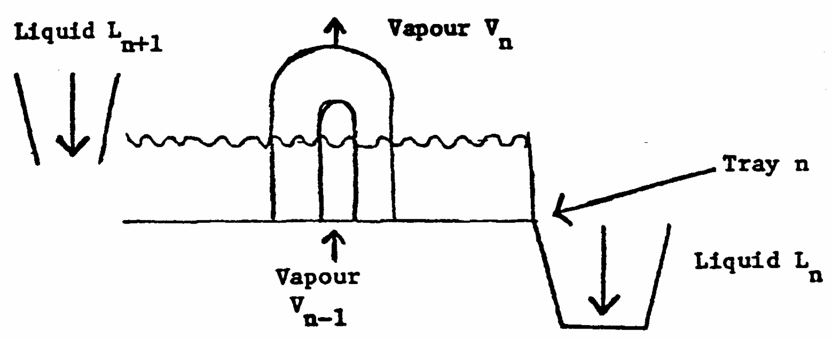


Figure 7.1: Distillation Tray

Let us consider the equilibrium relationships around this tray. The liquid leaving tray n is in equilibrium with the vapour leaving it. Thus, if we have a component such as C_3 we can write the equation for tray n:

Equation 7-1

$$Y_{C_3} = Kx_{C_3}$$

where:

Y_{C_3} = mole fraction of C_3 in vapour.

x_{C_3} = mole fraction of C_3 in liquid.

K = equilibrium constant.

If we know the temperature and pressure on the tray we can calculate the composition of one phase if we know the other. We also have a mass balance and generally a molar balance as follows:

Equation 7-2

$$L_{n+1} + V_{n-1} = V_n + L_n$$

where:

L_n = Moles of liquid from tray n.

V_n = Moles of vapour from tray n.

V_{n-1} = Moles of vapour to tray n.

L_{n+1} = Moles of liquid to tray n.

In the ideal stage concept the rate of mass transfer is only considered by the approach to equilibrium that the actual stage obtains as compared to that theorectically possible. This is normally expressed as efficiency.

We also have stages in such apparatus as leaching tanks, etc., in the mining industry.

Continuous Transfer

This occurs in packed towers, etc. Rate Equation - the general rate equation of:

$$Rate = \frac{Driving\ Force}{Resistance}$$

In general the driving forces are concentration differences while the resistances are normally film thicknesses. A difference of concentration exists only when a system is not at equilibrium. For example, consider a system of ammonia and water, i.e. pure ammonia and pure water brought together. Since ammonia dissolves in water, there is a driving force of a difference in concentration between the ammonia in the vapour and in the water. This is a very quick action.

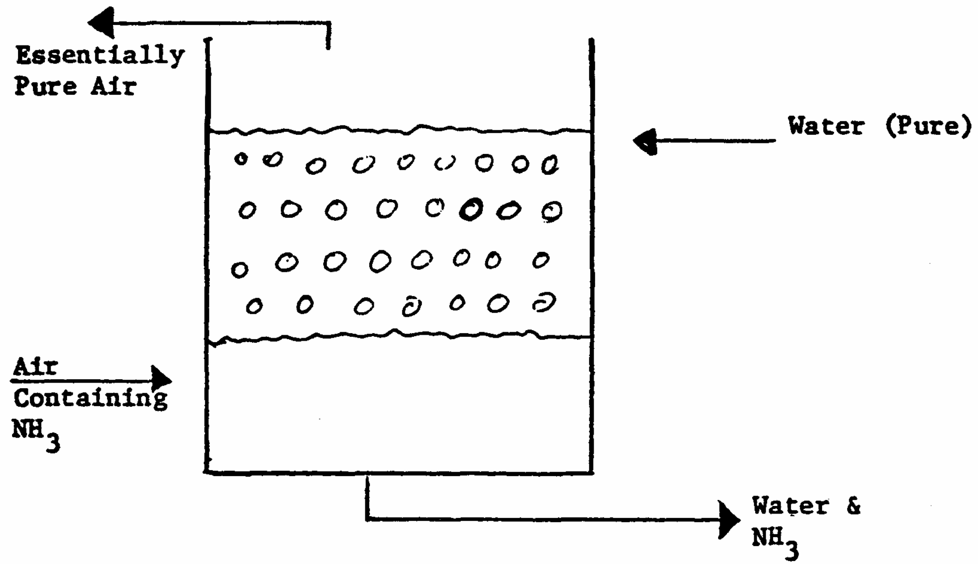


Figure 7.2: Mass Transfer System

Let us also consider a slow action, that of water in a pan outside on a dry day. Water evaporates because there is a driving force from pure water to the amount of water that the air can hold. This is, again, mass transfer.

Batch Transfer

In both previously discussed cases we have a continuous process in which the transfer is from the main bulk of one fluid through the interphase between the two fluids to the main bulk of the other fluid. In adsorption we have a slightly different case. The components are transferred from the main fluid to the surface of the other fluid, not to the main body.

The process continues until surface is saturated and then break-through occurs, i.e. concentration difference between passing gas and surface no longer great enough for transfer to completely take place.

7.2 Types of Diffusion

Two types of diffusion from one phase to the other are:

7.2.1 Molecular Diffusion

This is movement from one phase to the other or, in a single phase, by means of the molecules' thermal energy, i.e. have a beaker of water and add ink slowly or the evaporation of water in air.

7.2.2 Eddy Diffusion

By means of agitation you can increase diffusion rate extensively, i.e. stir beaker above, equilibrium comes much quicker. Of course, within each eddy, uniformity of concentration is achieved by molecular diffusion which is the ultimate process. One can see, therefore, that molecular diffusion is the mechanism of mass transfer in stagnant fluids, or in fluids that are moving in laminar motion - although it is, nevertheless, always present in highly developed turbulent flow.

7.3 Rate of Diffusion

We have seen from the simple demonstration that as long as there is non-uniformity (of concentration) in a given solution, the solution is spontaneously brought to uniformity by diffusion, the solute molecules moving from a place of high concentration to one of low concentration. The rate at which the solute molecules move at any point, in any direction, must, therefore, depend on the concentration gradient at that point. This rate can be conveniently described in terms of a molar flux or:

moles/(time) (area)

the area being measured in a direction normal to the diffusion. For non-reacting systems of two components A and B, the molar fluxes of A and B are described by Fick's Law of Diffusion, which may be written for steady one dimensional transfer as:

Equation 7-3

$$J_A = -D_{AB}\frac{dC_A}{dZ}$$

Equation 7-4

$$J_B = -D_{BA}\frac{dC_B}{dZ}$$

where:

J_A and J_B = molar fluxes of A and B relative to the molar average velocity of the mixture.

Z = distance in the direction of diffusion

C_A & C_B = molar concentrations of A and B

D_{AB} and D_{BA} = molecular diffusivities of A in B and B in A respectively.

Now for a perfect gas:

$$C_A = \frac{P_A}{RT} \quad and \quad C_B = \frac{P_B}{RT}$$

where:

P_A and P_B = partial pressures of A and B

R = gas constant

T = absolute temperature

So that equations (3) and (4) become

Equation 7-5

$$J_A = -\frac{D_{AB}}{RT}\frac{dP_A}{dZ}$$

Equation 7-6

$$J_B = -\frac{D_{BA}}{RT}\frac{dP_B}{dZ}$$

where:

J = flux relative to average mole velocity of mixture.

The negative sign in equations (3) to (6) emphasizes that diffusion occurs in the direction of a drop in concentration. Molecular diffusivity (D_{AB} or D_{BA}) is a characteristic of a constituent and its environment (i.e. temperature, pressure, concentration, state of aggregation, etc.). The kinetic theory yields several theoretical expressions of the following form, for the binary gas systems.

The following equation is recommended for estimating diffusion coefficients in binary gas systems at pressures less than 500 psia:

Equation 7-7

$$D_{1,2} = \frac{0.04381 T^{1.5}\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^{0.5}}{p(\sigma_{1,2})^2\,\Omega_D}$$

where:

$D_{1,2}$ = diffusion coefficient of component 1 in component 2 in square feet per hour.

T = temperature, in degress Rankine.

M_1, M_2 = molecular weights of components 1 and 2, respectively.

p = pressure, in pounds per square inch absolute.

$\sigma_{1,2}$ = arithmetic average of the collision diameters for 1,2 components 1 and 2, in angstrom units.

Ω_D = collision integral for diffusion.

Procedure to find "D"

1. Obtain the Lennard-Jones force constants (ε/k and σ) for both components of the mixture from the Table in API data book.

   If the compounds of interest are not listed, use equations 8 and 9 in the API data book with the critical temperature and volume listed in Chapter 1 and the critical compressibility factor in Chapter 2 of the API data book:

Equation 7-8

$$\frac{\varepsilon}{k} = 65.3 T_C Z_C{}^{3.6}$$

where:

ε/k = Lennard-Jones potential parameter, in degrees Rankine.

k = Boltzmann constant.

T_c = critical temperature, in degrees Rankine.

Z_c = critical compressibility factor.

Equation 7-9

$$\sigma = 0.7402 \frac{(MV_C)^{0.333}}{z_C{}^{1.2}}$$

where:

σ = Lennard-Jones collision diameter, in angstrom units.

M = molecular weight.

V_c = critical volume, in cubic feet per pound. c

2. Calculate the Lennard-Jones force constants for the mixture with equations (10) and (11):

Equation 7-10

$$\sigma_{1,2} = \frac{1}{2}(\sigma_1 + \sigma_2)$$

where:

subscripts 1 and 2 refer to the components and 1,2 refer to the mixture.

Equation 7-11

$$\frac{\varepsilon_{1,2}}{k} = \left[\left(\frac{\varepsilon_1}{k}\right)\left(\frac{\varepsilon_2}{k}\right)\right]^{0.5}$$

3. Calculate the dimensionless group, $kT/\varepsilon_{1,2}$ using the $\varepsilon_{1,2}/k$ result from equation 11 and the temperature of interest in degrees Rankine. Using this value, interpolate the collision integral, Ω_D from Table in API data book.
4. Calculate the diffusion coefficient using equation (7).

Note: The following equation is recommended for estimating diffusion coefficients in dilute liquid binary solutions. The equation may be used directly or approximated conveniently with a nomograph, Fig. 13A1.2 in the API data book.

Equation 7-12

$$D_{1,2} = \frac{1.59x10^{-7}\left(\Psi_2\ M_2\right)^{0.5T}}{\mu\left(\frac{M_1}{\rho_1}\right)^{0.6}}$$

where:

$D_{1,2}$ = diffusion coefficient of solute (component 1) in solvent (component 2), in square feet per hour

Ψ_2 = association parameter for the solvent

M_2 = molecular weight of the solvent

M_1 = molecular weight of the solute

T = temperature, in degrees Rankine

μ = viscosity of the solution, in centipoises

ρ_1 = saturated liquid density of the solute at the normal boiling point, in grams per milliliter

Procedure

1. Obtain M_1 and M_2 from Chap. 1, and obtain ρ_1 using the methods or figures in Chap. 6. In the absence of experimental data, estimate μ using chap. 11 procedures. (All chapters refer to API Data Book).
2. Determine the association parameter for the solvent, Ψ_2 = 1. For other associated solvents not listed in the following table, estimate a value between 1.0 and 2.6 based on the relative associative tendency of the solvent:

Solvent	**Ψ_2**
Nonassociated solvents	1.0
Ethyl alcohol	1.5
Methyl alcohol	1.9
Water	2.6

3. Obtain $D_{1,2}$ directly from equation 12 or with the nomograph, Fig. 13A1.2 in the API data book.

Going back to equations (5) and (6), we can consider first the general case in which a steady bulk flow is imposed upon the fluid mixture in the direction in which component A is diffusing. The magnitude of this molar flux of the mixture relative to stationary coordinates will be:

$N_A + N_B$

The flux of components A and B relative to stationary coordinates are now the resultant of two quantities (vectors):

1. The flux caused by the bulk flow.
2. The flux caused by molecular diffusion.

Whereas these vectors are in the same direction for component A, they are clearly in the opposite direction for component B. The total flux of A relative to stationary coordinates, then, is the sum of that resulting from the bulk flow and that due to molecular diffusion (i.e. for a gaseous mixture).

Equation 7-13

$$N_A = (N_A + N_B)\frac{P_A}{P} - \frac{D_{AB}}{RT}\frac{dP_A}{dZ}$$

Two special cases of molecular diffusion are customarily considered:

1. Equimolal Counterdiffusion.
2. Unimolal Unidirectional Diffusion.

In the case of equimolal counter diffusion (process often approximated in the distillation of binary systems) the total molal flux with respect to stationary coordinates is zero (A and B diffusing in the opposite direction and at the same molal rate) so that:

$N_A = -N_B$

then from equations (5), (6) and (7)

Equation 7-14

$$N_A = J_A = -N_B = -J_B$$

but $P_A + P_B = P = constant$

therefore

Equation 7-15

$$\frac{dP_A}{dZ} = -\frac{dP_B}{dZ}$$

and from equations (5), (6) and (14)

Equation 7-16

$$D_{AB} = D_{BA} = D$$

At steady state N_A and N_B are constants, so that equations (5), (16) and (13) may be combined and integrated for constant D to give:

Equation 7-17

$$N_A = \frac{D}{RTZ}\left(P_{A_1} - P_{A_2}\right)$$

(steady stage equimolal counterdiffusion)

also for liquids:

$$N_A = \frac{D_{AB}}{Z}\left(C_{A_1} - C_{A_2}\right)$$

where:

$Z = Z_1 - Z_2$

P_{A_1} and P_{A_2} = partial pressures of A at Z_1 and Z_2 respectively.

C_{A_1} and C_{A_2} are in concentration at Z_1 and Z_2.

For the case of steady state unimolal, unidirectional diffusion in gases, the flux of component B in one direction, because of the bulk flow, is equal to the flux of B in the opposite direction because of the molecular diffusion. Component B is therefore motionless in relation to stationary coordinates and $N_B = 0$. In such as case:

Equation 7-18

$$N_A = \frac{DP}{RTZ} \ln\left(\frac{P_{B_2}}{P_{B_1}}\right)$$

which may be written as:

Equation 7-19

$$N_A = \frac{DP}{RTZ}\left(\frac{P_{B_2} - P_{B_1}}{P_B \log mean}\right)$$

or

Equation 7-20

$$N_A = \frac{D}{RTZ}\left(\frac{P}{P_B \log mean}\right)\left(P_{A_1} - P_{A_2}\right)$$

(unimolal, unidirectional diffusion)

where

$$P_B \log mean = \frac{P_{B_2} - P_{B_1}}{\ln \dfrac{P_{B_2}}{P_{B_1}}}$$

7.4 Mass Transfer Coefficients

Consider the distribution of a solute (A) between two immiscible phases in contact with each other, as represented by the figure below:

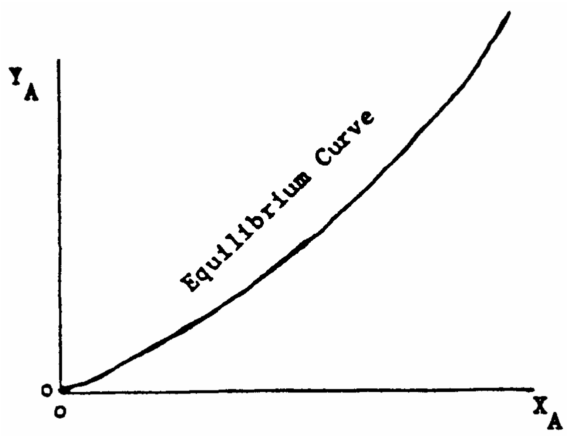


Figure 7.3: Mass Transfer Curve

The first phase may be gaseous and the second phase liquid. Y_A will then denote the composition of the gas phase and X_A the composition of the liquid phase.

A point on the equilibrium curve gives the equilibrium compositions of the two phases. A point located above the curve indicates that component A is being transferred from the gas to the liquid and a point below the curve indicates that component A is being transferred from the liquid to the gas.

It is assumed that local equilibrium prevails at the interface where the compositions are Y_A^* and X_A^*. If transfer takes place from the gas to the liquid, the individual mass transfer coefficients k_g and k_L, for the gas and liquid phases respectively, can be defined as follows:

Equation 7-21

$$N_A = k_g\left(Y_A - Y_A^*\right)$$

where

Equation 7-22

$$k_g = \frac{D_{AB}}{RTZ}$$

Equation 7-23

$$N_A = k_L\left(X_A^* - X_A\right)$$

where

Equation 7-24

$$k_L = \frac{D_{AB}}{Z}$$

where:

Y_A and X_A are the concentrations of component A in the bulk of gas and liquid phases.

Let us consider what happens in the above transfer as shown in Figures 7.4 and 7.5. Equations (21) and (23) show that

Equation 7-25

$$\frac{Y_A - Y_A^*}{X_A - X_A^*} = -\frac{k_L}{k_g}$$

Interfacial concentrations X_A^* and Y_A^* are often unknown and frequently impossible to determine at a given location at the interface and it is then more convenient to use overall coefficients K_g and K_L, defined in terms of overall concentration differences as shown below:

Equation 7-26

$$N_A = K_g\left(Y_A - Y_{AL}\right)$$

Equation 7-27

$$N_A = K_L\left(X_{AG} - X_A\right)$$

The locations of Y_{AL} and X_{AG} are shown in the figures. There are respectively Y_{AL} the equivalent of X_A in terms of Y and X_{AG} the equivalent of Y_A in terms of X.

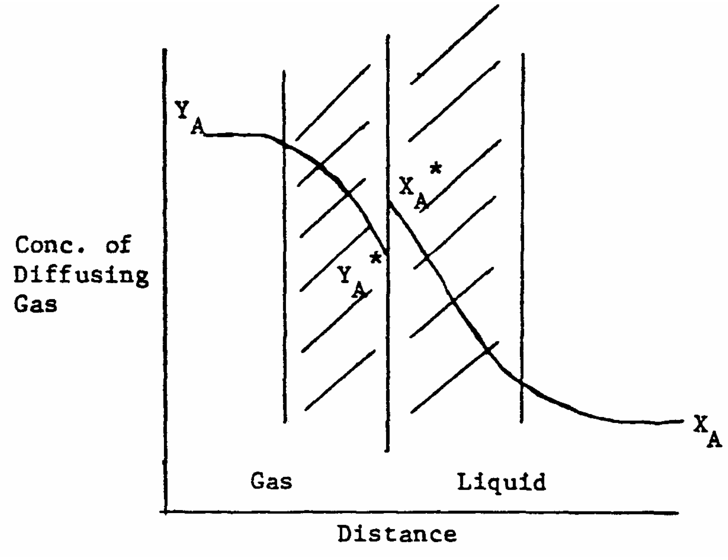


Figure 7.4: Mass Transfer Across Film

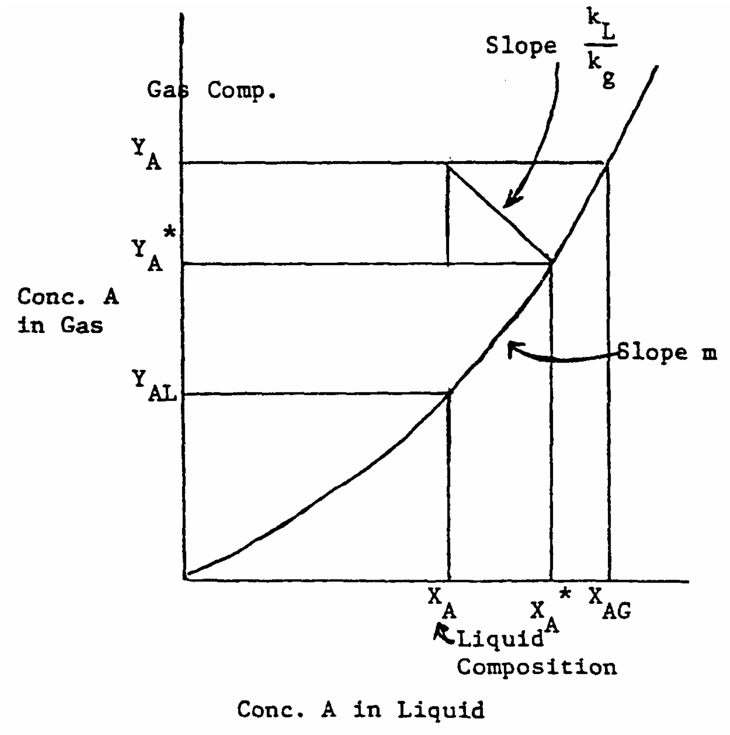


Figure 7.5: Mass Transfer Curve

The relationships between the individual coefficients of equations (21) and (23) and the overall coefficients of equations (26) and (27) are shown in the following equations:

Equation 7-28

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{m}{k_L}$$

Equation 7-29

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{m k_g}$$

and

Equation 7-30

$$\frac{1}{K_g} = \frac{1}{m K_L}$$

where:

m = the slope of the equilibrium curve.

when:

$\frac{1}{k_g} = \frac{m}{k_L}$ gas phase is controlling when:

$$\frac{1}{k_L} = \frac{1}{mk_g}$$ liquid phase is controlling

The total interfacial area (A) for mass transfer in a column is usually not known and in such cases mass transfer rates are frequently based on unit volume of the equipment instead of the unit interfacial area. The rate equations are then modified to the following form:

Equation 7-31

$$N_A\,A = k_g\,a\left(Y_A - Y_A^*\right)V_0 = k_L\,a\left(X_A^* - X_A\right)V_0 = K_g\,a\left(Y_{AG} - Y_{AL}\right)V_0 = K_L\,a\left(X_{AG} - X_{AL}\right)V_0$$

where:

V_O = the volume of the tower

a = interfacial area per unit volume (assumed value)

7.5 Review of Processes Depending on Ideal Stages

Now let's consider three mass transfer operations that depend primarilty for analysis on the ideal stages.

7.5.1 Distillation

In this process different compounds are separated by the application of heat to transfer the more volatile components from the liquid to the gas. A continuing process of vapourization and condensation takes place in distillation until relatively pure top and bottom products are obtained.

The difficulty in separation can be roughly measured by the difference in boiling points of compounds at atmospheric pressure, i.e.

Table 7.1: Boiling Points for Light Hydrocarbons

propane	-43.7°F	(-42°C)
isobutane	+10°F	(-12.2°C)
n butane	31.1°F	(-0.5°C)
isopentane	82.1°F	(27.8°C)
n pentane	96.9°F	(36.0°C)
n hexane	155.7°F	(68.6°C)

This shows that the separation between C_3 and iC_4 is easier than between iC_5 and nC_5. A more accurate measure of the difficulty of separation is the relative volatility which is expressed as α

Equation 7-32

$$\alpha = \frac{K_l}{K_n}$$

where:

K_ℓ = equilibrium constant of the light key component and K

K_n = equilibrium constant for the heavy key component concerned in the separation, both at the same temperature and pressure.

The key components in multicomponent separation are those components that are being separated. The components appear in both the top and bottom of a column, the light key appears mostly in the top and slightly in the bottom, i.e. it is the lightest component in the bottom. The converse is true of the heavy key. It appears primarily in the bottom and is the heaviest component in the top.

7.5.2 Absorption

In this operation a soluble component in the gas phase is dissolved in the liquid phase. This is done by either physical absorption or by chemical reaction.

7.5.3 Stripping

This is the opposite of absorption. That is, it is the removal by the application of heating or by the application of a lean gas of the soluble liquid components. It is actually distillation when heat is applied to generate the stripping medium.

7.5.4 Terms Used

Let's review some terms involved in distillation, absorption and stripping.

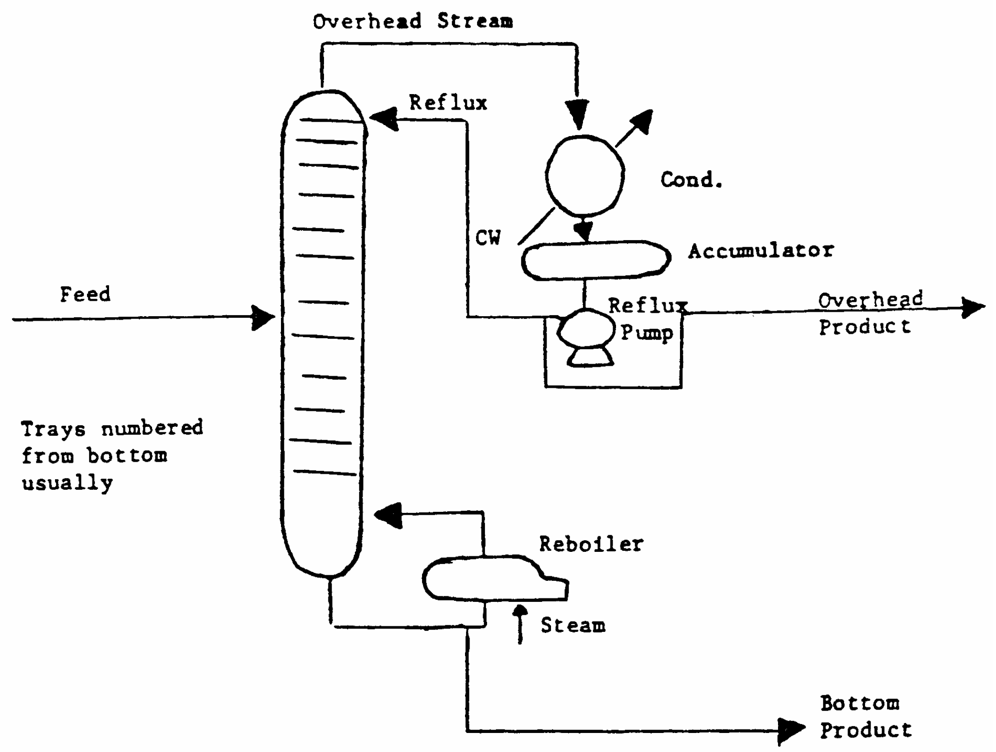


Figure 7.6: Typical Distillation System

7.6 Equipment

Let us now consider the type of equipment used for these operations. Primarily these operations are conducted in tall towers filled with trays or plates or packing. The oil industry relies more on trays rather than packing for large diameter towers and packing for small diameter towers (24" or less) [60cm or less]. The chemical industry uses packed towers of much greater diameter. Packed towers are coming more into use in the oil industry.

7.6.1 Tray Types

Let us consider the operation of a tray in a tower.

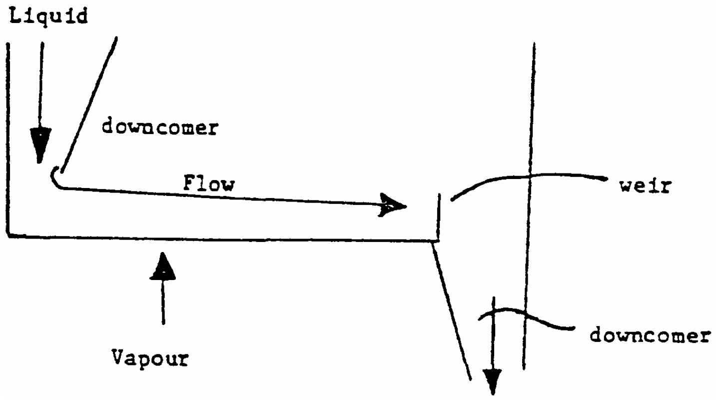


Figure 7.7: Flow Across a Tray

The object of the tray is to make sure liquid and gas come in intimate contact and have the opportunity to reach as close as possible to equilibrium. The prime example of obtaining this contact is with the bubble cap.

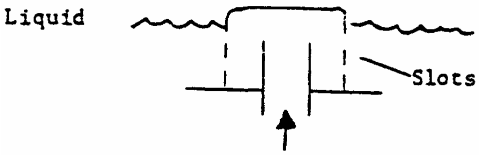


Figure 7.8: Bubble Cap Tray

Another common tray is the valve tray

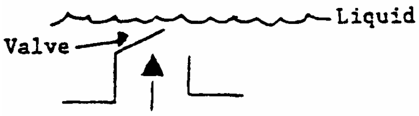


Figure 7.9: Valve Tray

Sieve trays are a series of perforated holes in which both gas and liquid can pass through or just have the gas going up and the liquid going down a downcomer as in the previous type of trays.

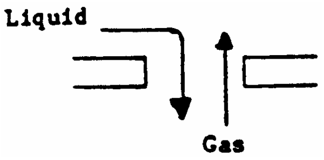


Figure 7.10: Sieve Tray

There are also such trays as turbo girds which are similar to sieves; side to side pans; disc and doughnut trays; uniflux trays; ripple trays; Linde trays. The chief object is to get good contact. The operation of various types of contacting devices on trays and the limits on tray operation are shown on Page 21a which are reproduced from the new English GPSA Data Book.

7.6.2 Tray Selection

Type of tray depends on service. The sieve tray normally has the greatest capacity with least flexibility in service. The operating range is limited because of weeping. Also there can be serious problems in corrosive or fouling services. The floating valve cap tray has the next greatest capacity and a wider range of operation. It can be designed so that it cannot shut in fouling service.

The bubble cap tray is the old standby but is being replaced with other higher capacity trays. It is still quite widely used, however. A summary of trays used in gas processing is as follows:

MEA, DEA and other sweetening solvents

All new towers, valve trays. *

Condensate Stabilization

All new towers, valve trays

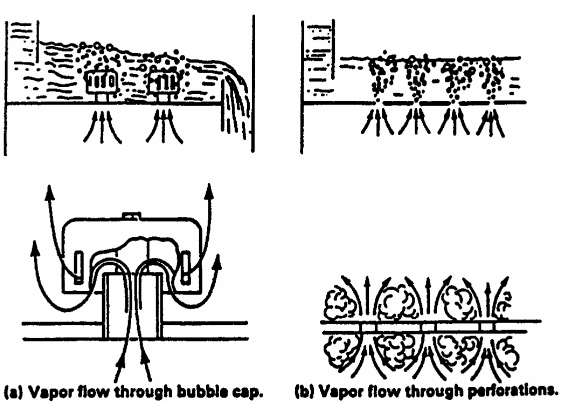
LPG Fract.

Sieves quite often

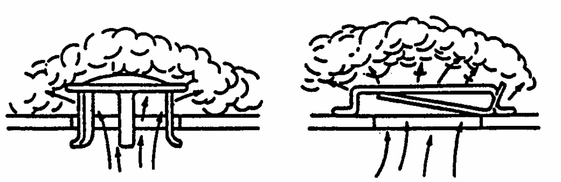
* Sieve trays used for hot pot in one case and intalox saddles in another. Sieve trays used in Old Plants.

7.6.3 Detailed Tray Diagrams

Flow Through Vapor Passages

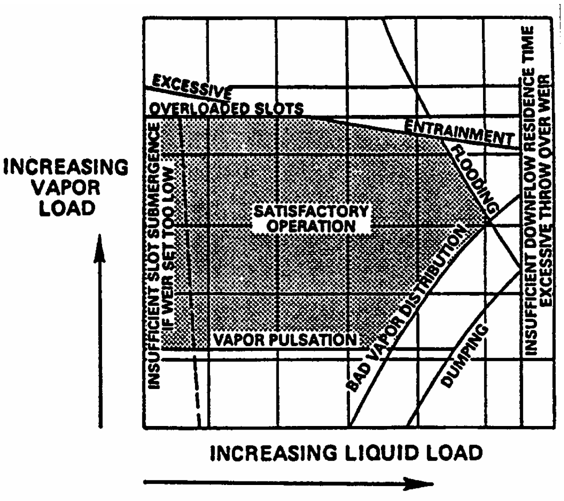


(a) Vapor flow through bubble cap. **(b) Vapor flow through perforations.**

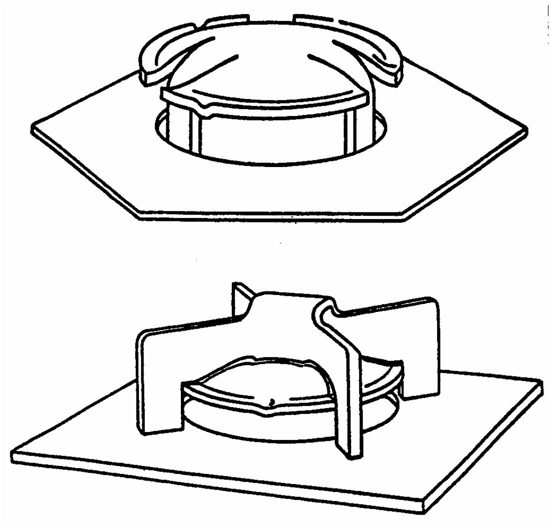


(c) Vapor flow through valves.

Limits of Satisfactory Tray Operation for a Specific Set of Tray Fluid Properties



Valve Trays



Top Two Trays of a Bubble-cap Column

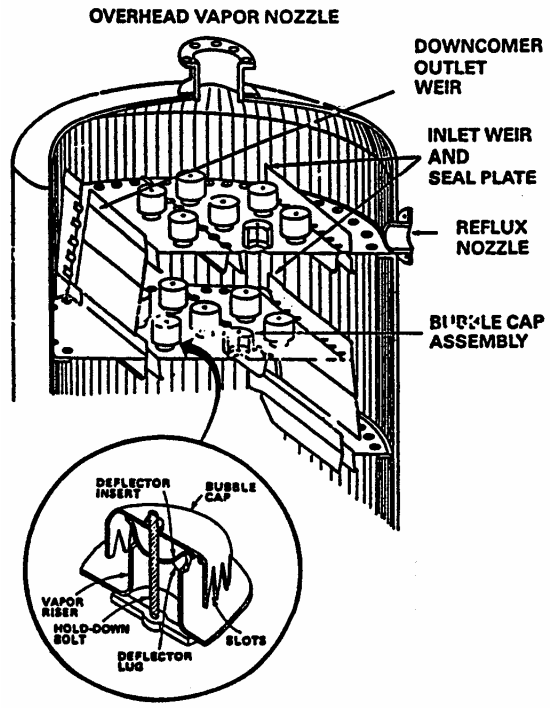


Table 7.2: Comparison of Tray Types

Type	Capacity	Turndown	Efficiency	Cost
Bubble	Third	1st & 2nd	Third	Third
Valve	Second	1st & 2nd	Second	Second
Sieve	First	Third	First	First

Revised from Kitterman & Ross[2]

7.6.4 Packing

The other type of contacting device widely used is packing. Packing provides extensive surface for liquid and gas contact. Packing is usually made of ceramic, metal or carbon shapes to give extensive surfaces. The names of the common shapes are:

1. Raschig ring
2. Intalox saddle
3. Berl saddle
4. Pall rings (Flexi rings are like pall rings)

The pall ring is considered to be the most efficient packing at present. Eckert[19] gives a good review of different packings. Figure 7.7a shows a typical packed tower and packing shapes.

7.7 Tower Sizing - Trayed Towers

7.7.1 General

There are two problems process wise in tower sizing. These are the tower diameter and the tower height. The tower height is dependent on the actual number of stages required for a separation and the distance apart these stages are. The number of stages depends on whether distillation or absorption is to be practised. The determining of these number of stages will be discussed shortly. However, the tower diameter is not particularly a function of the transfer process but primarily a function of the gas and liquid load and the tower internals.

7.7.2 Diameter Determinations

7.7.2.1 Entrainment

This is the carryover of liquid particles from one stage to another. Entrainment is caused by high gas velocity and towers that are gas loaded are generally limited by entrainment.

7.7.2.2 Flooding

This occurs primarily whenever the downcomers fill up with liquid and any change of liquid or gas flow causes very erratic performance, high pressure drops and packing of the tower. This occurs primarily with liquid loaded towers, however the flooding point is a function of both liquid and gas rates.

7.7.2.3 Gas Loaded Towers

Towers are generally either gas or liquid loaded. For gas loaded towers the old Brown & Souders[3] equation can be used:

Equation 7-33

$$v = K\sqrt{\frac{\rho_L - \rho_V}{\rho_V}}$$

where:

v = the allowable superficial velocity (empty tower) ft/sec

ρ_L = density of liquid at tower conditions

ρ_V = density of vapour at tower conditions

K = a constant

Or

Equation 7-34

$$G_{\max} = C\sqrt{\rho_V\left(\rho_L - \rho_V\right)}$$

where:

G_{max} = allowable mass superficial velocity lb/ft^2/hr

C = a constant, given in Figure 7.11,

which depends on the surface tension of the liquid in the tower and the distance between the plates. Values for K are given in Perry. For a 24 inch tray spacing the value of K varies from 0.15 to 0.18. For example a test on a 6 ft diameter absorber with bubble caps was conducted. Here are the data obtained:

Brown & Souders allowable gas velocity was 69.6 MMSCD

Bubble cap allowable velocity per article by Zenz was 85.3 MMSCFD

Actual Test (based on when significant entrained occurred) was 84.2 MMSCD

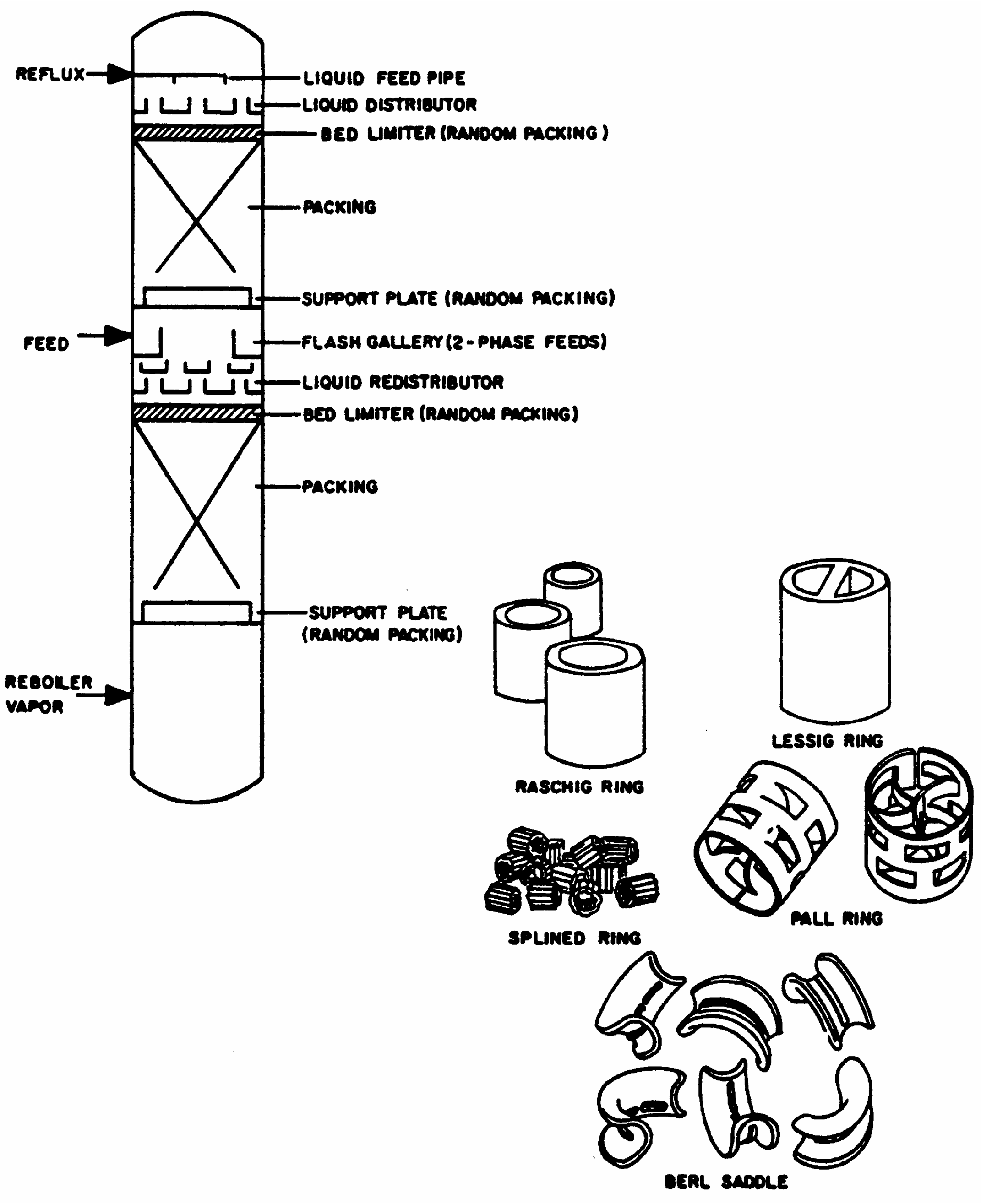
Use the previously given equations and data to give approximate diameter. For exact size the present practice is to specify the vapour and liquid loading, both maximum and minimum, the process and operating conditions, etc., and allow the tray manufacturer to select the tray size and tower diameter for you.

Koch, Clitsch, and Nutter (tray manufacturers) have prepared design manuals for tower sizing for English and metric calculations.

To use the data given here it is probably easiest to calculate v and G in English units and then convert to m/sec or kg/hr m^3 respectively. This applies through tower diameter determination.

Section 19 of the most recent English GPSA Data book gives a good review on tower capacities and calculations of same.

Typical Packed Tower Layout and Common Packing Types



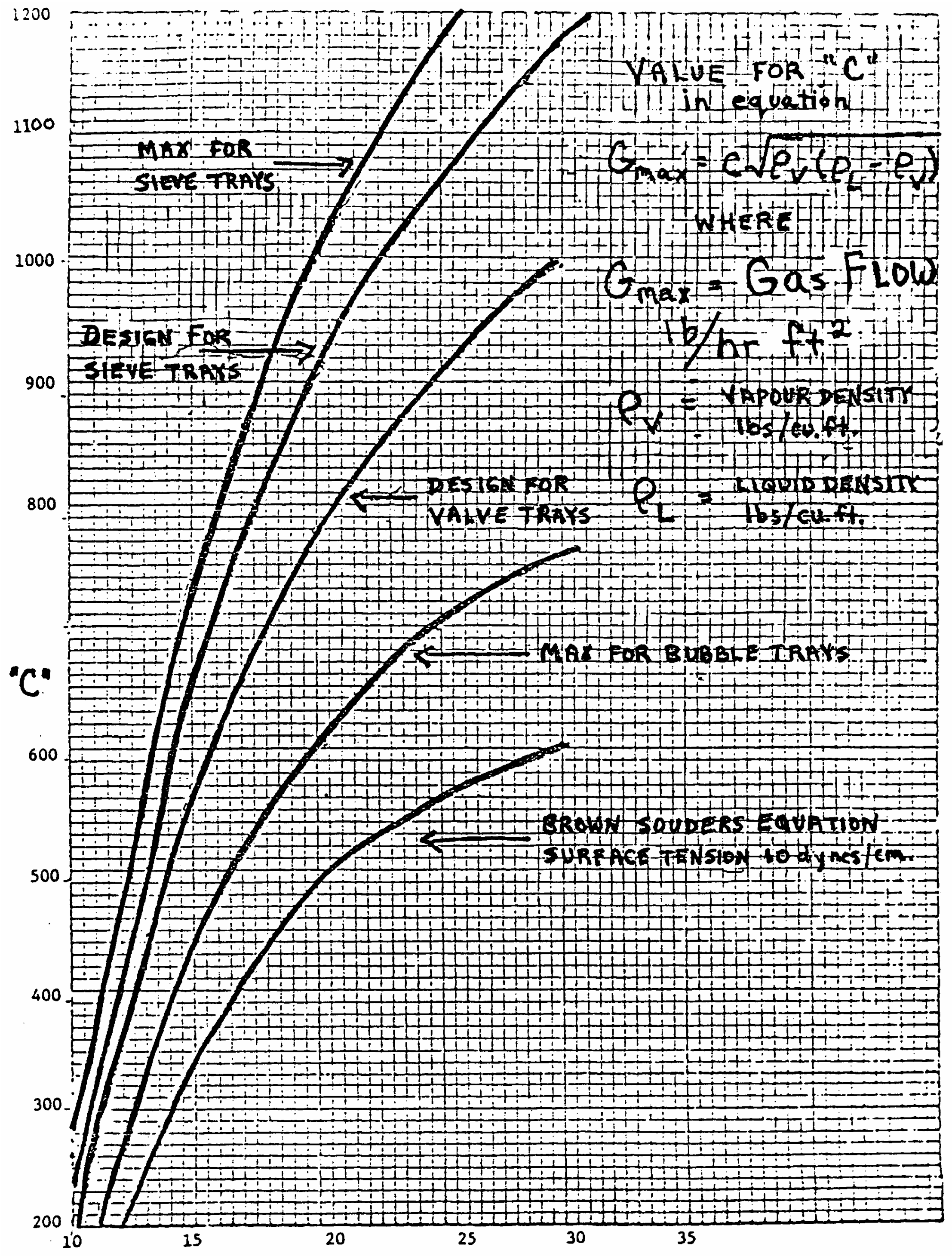


Figure 7.11: Tray Capacities

7.7.2.4 Liquid Loaded Towers

In liquid loading the prime consideration is the liquid backup in downcovers, that is the height of liquid in a downcomer.

Old recommended values have been 50% of downcomer full of liquid for ordinary services and 35% for foaming service. However, many towers have been operated at 60% without instability so it is recommended 50% be used all the time. The height of the liquid in a downcomer can be calculated as outlined below and is related to all the other pressure drops on a tray. This is a simplification but is generally accurate. In general the height of liquid in the downcomer can be calculated from the following equation:

Equation 7-35

$$h = 2\left(h_w + h_{ow}\right) + h_v + h_D$$

where:

h = the height of clear liquid in downcomer.

h_w = height of weir.

h_{ow} = height of liquid over weir.

h_v = pressure drop due to vapour flow through tray.

h_D = pressure drop due to liquid flow under down spout.

Downcomer maximum design liquid load is about 200 bbls/ft^2/hr or 0.3 ft/sec velocity. Downcomer should not normally take up more than 15% of tower cross-sectional area.

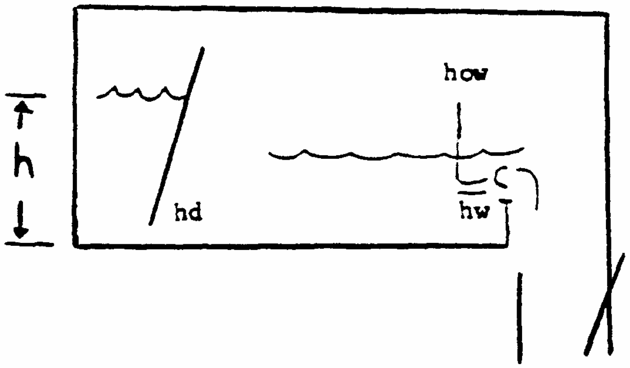


Figure 7.12: Hold Up on Tray

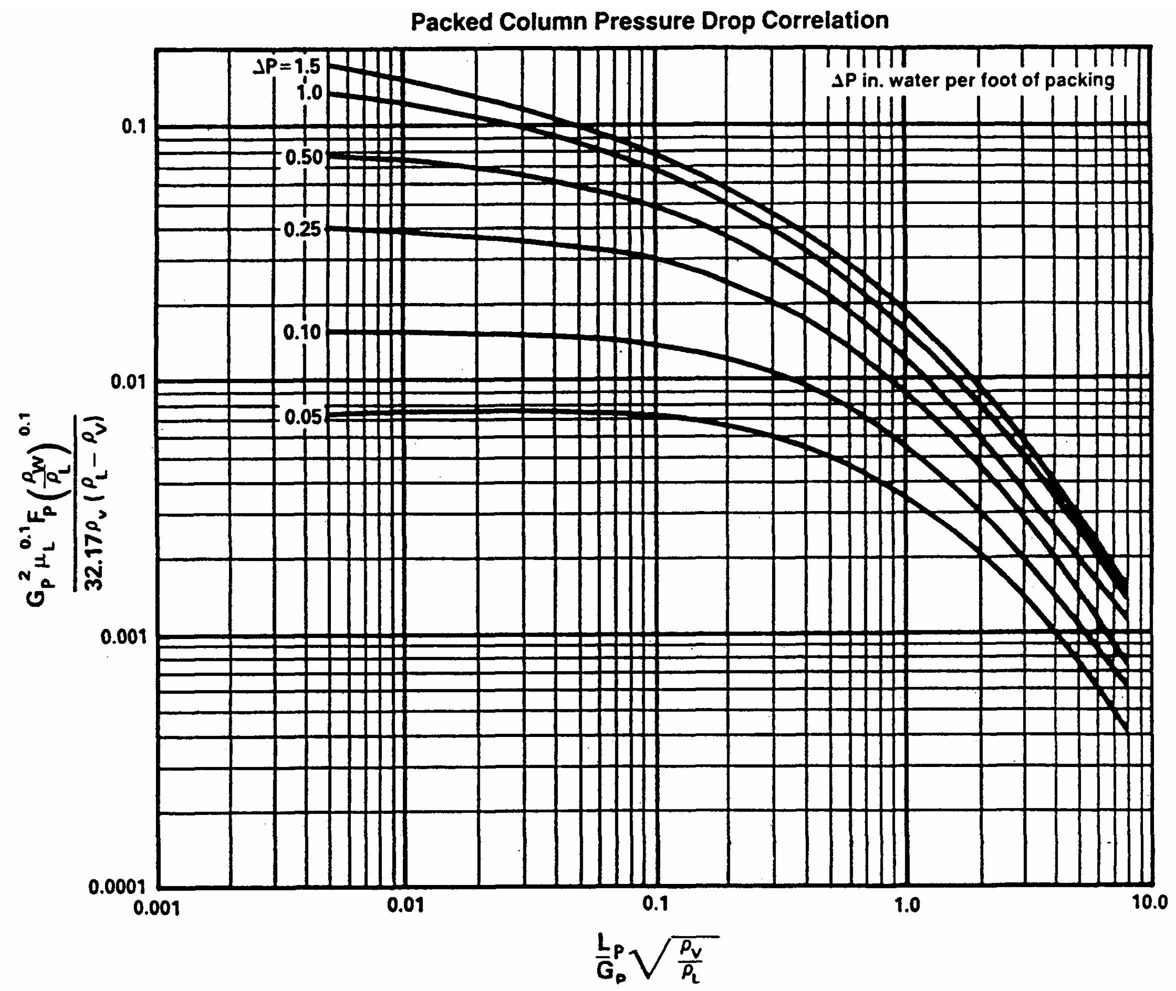


Figure 7.13: Packed Tower Correlation

7.8 Tower Sizing Packed Columns

For the design of packed columns the generalized pressure drop correlation can be used. It is a plot of the gas flow multiplied by several factors pertaining to the type of packing and the fluids being fractionated against a liquid to gas ratio. This plot is given in Figure 7.13. This plot is shown in Perry, The U.S. Stoneware Book. This correlation shows pressure drop lines. The design procedure is to size the tower to operate at about 80% of flooding which is about 0.25 to 0.5 inch of H_2O/ft. For foaming solutions use 0.1 inch of H_2O/ft of packing.

Figure 7.13 is a plot of:

Equation 7-36

$$\left(\frac{L_p}{G_p}\right)\left(\frac{\rho_V}{\rho_L}\right)^{1/2} \quad versus \quad \frac{G_p^2\,\mu_L^{0.1}\,F_p\left(\frac{\rho_W}{\rho_L}\right)^{0.2}}{32.17\,\rho_V\left(\rho_L-\rho_V\right)}$$

where:

L = liquid mass flow lb/hr/ft^2

G = gas flow mass velocity lb/hr/ft^2

ρ_v = gas density lb/ft^3

ρ_L = liquid density lb/ft^3

ρ_w = density of water

μ_L = liquid viscosity in centipoise

F_p = packing factor as given in the following table

Table 7.3: Packing Characteristics

Packing Factors (F_p) - (DUMPED PACKING)

Packing Type	Material	Nominal Packing Size (inches)										
		1/4	**3/8**	**1/2**	**5/8**	**3/4**	**1**	**1.25**	**1.50**	**2**	**3**	**3.5**
IMTP®	Metal				51		40		24	18	12	
Hy-Pak™	Metal						45		29	26		16
Super Intalox Saddles®	Ceramic						60			30		
Super Intalox Saddles®	Plastic						40			28		18
Pall Rings	Plastic				75		55		40	26		17
Pall Rings	Metal				70		56		40	27		18
Intalox Saddles®	Ceramic	725	330	200		145	92		52	40	22	
Raschig Rings	Ceramic	1600	1000	580	380	255	155	125	95	65	37	
Raschig Rings	1/32" Metal	700	390	300	170	155	115					
Raschig Rings	1/16" Metal			410	300	220	144	110	93	62	32	
Berl Saddles	Ceramic	900		240		170	110		65	45		

Here are some very approximate inch height of equivalent theoretical plate (HETP) for Pall Rings.

Packing Size	HETP
5/8"	6" to 12"
3/4"	12" to 18"
1"	18" to 24"
1 1\2"	24" to 30"
2"	30" -

7.9 Tower Height - Distillation

7.9.1 General

In this case we are trying to separate the more volatile component from a less volatile component. To find the height of the equipment we wish to find the number of trays or the height of packing. Let us first review some phase diagrams for two component systems. The temperature composition diagram for a two component ideal system at constant pressure can be shown as follows:

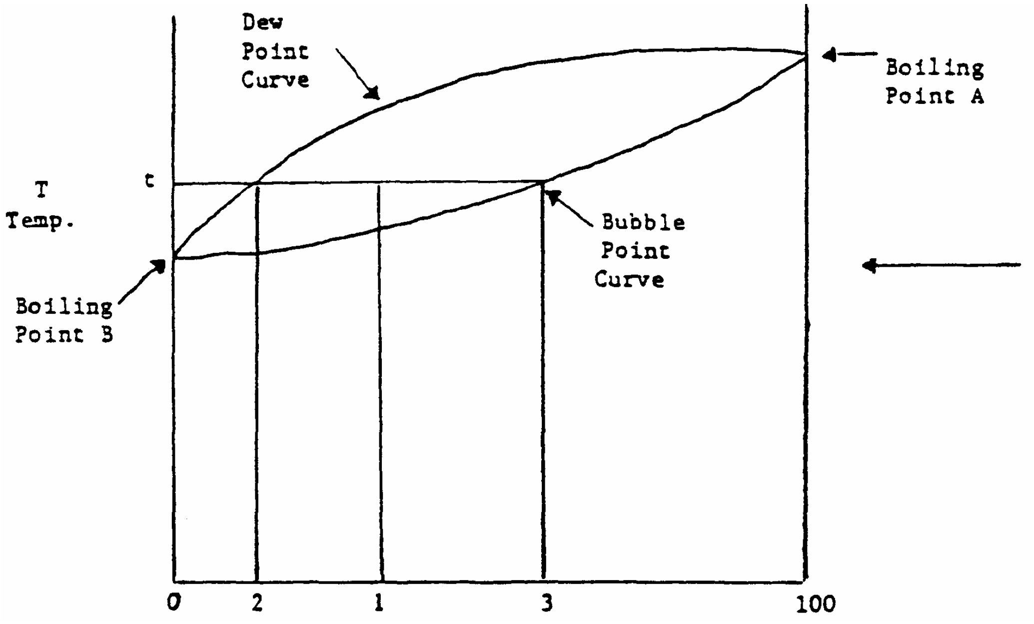


Figure 7.14: Temperature Composition Diagram for Two Components

Consider a system of composition 1 at temperature 't'. Two-phase exists, ie.vapour and liquid. The vapour would have a composition at 2, i.e. smaller amount of A than at 1 and greater amount of B than at 1. The liquid would have a composition of 3, i.e. more of A and less than B. This is how we can separate two components. Let us now see what a diagram of the relation between the composition of the gas phase and the liquid phase looks like. This, of course, is at constant pressure.

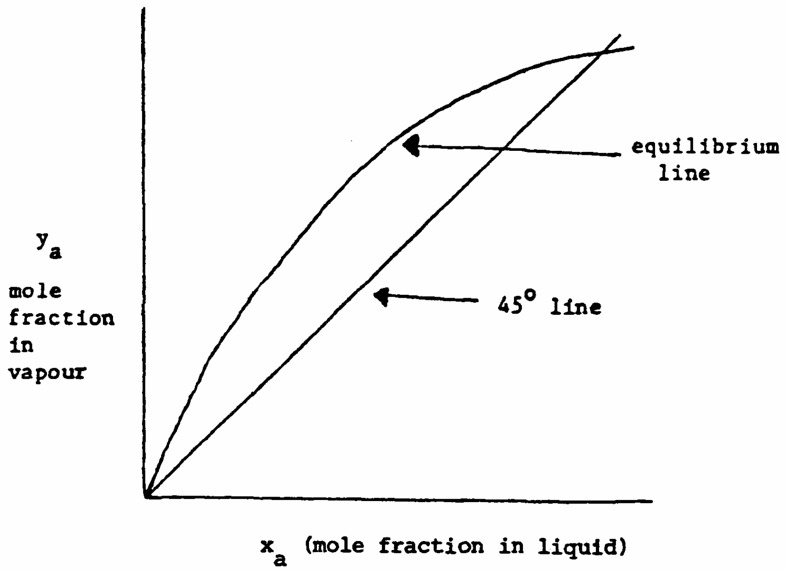


Figure 7.15: Vapour Liquid Composition Diagram

If the system is an ideal solution than Raoult's law applies, that:

Equation 7-37

$$PP_a = x_a \, VP_a$$

where:

PP$_a$ = partial pressure of A

VP$_a$ = vapour pressure of A

and an ideal gas in vapour phase, Dalton's law applies, i.e.

Equation 7-38

$$y_A = \frac{PP_a}{PT}$$

where:

PT = total pressure

then the vapour liquid line is expressed by

Equation 7-39

$$y_a = x_a \frac{VP_a}{PT}$$

or if we have K data

Equation 7-40

$$y_a = K_a \, x_a$$

7.9.2 Two Component Distillation

Let us consider the distillation of two components a and b. First of all let us consider a tower and its auxiliary components.

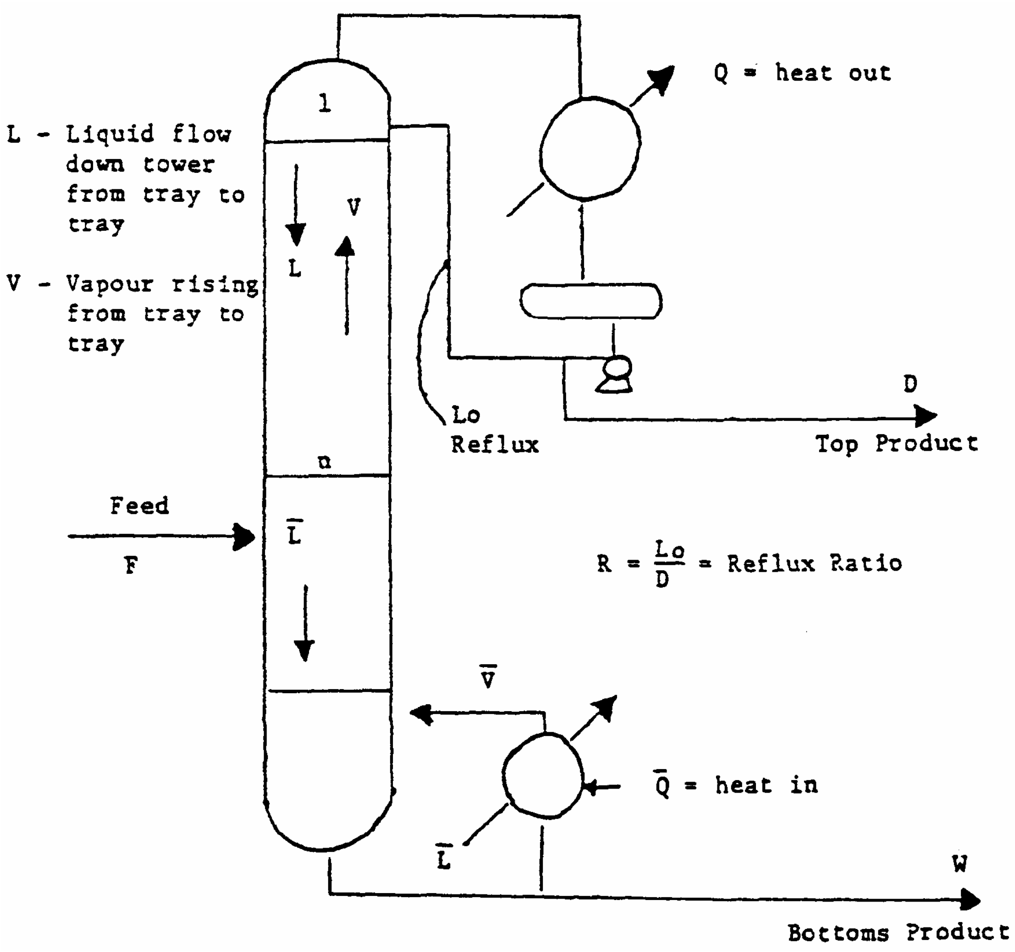


Figure 7.16: Typical Distillation System for Two Components

Consider:

y = vapour composition of a (mole fraction)

x = liquid composition of a (mole fraction)

z = feed composition of a (mole fraction)

7.9.3 McCabe Thiele[7] Method of Finding Number of Ideal Stages for a Two Component System

We make the following assumptions:

- Constant molal liquid flow down the tower to feed tray and then constant molal liquid below feed (but a different value).
- Similarly constant molal vapour flow in the two sections of the tower (but different in each section).
- There is not a significant heat of solution or a significant change in H_V - H_L throughout the tower.

The method is as follows:

1. First we take a vapour liquid diagram for component A (See Figure 7.14 and 7.19).
2. Assume vapour leaving tray n is in equilibrium with liquid leaving tray n.

For whole column for component:

Equation 7-41

$$F = D + W$$

where:

F = Feed in moles
D = Overhead product
W = Bottoms product

For a single tray:

Equation 7-42

$$V_{n+1} + L_{n-1} = V_n + L_n$$

or a component

Equation 7-43

$$V_{n+1}\left(y_{n+1}\right) + L_{n-1}\left(x_{n-1}\right) = V_n\, y_n + L_n\, x_n$$

And since we have constant molal vapour flow and liquid flow:

Equation 7-44

$$y_{n+1} + x_{n-1} = y_n + x_n$$

$$V = L + D = D\left(R + 1\right)$$

we know composition of X_D and X_W (products we wish).

3. We know that vapour from top tray $y_1 = X_D$. Plot on diagram, Fig. 7.19. First let us take a molal material balance around enriching section (top section).

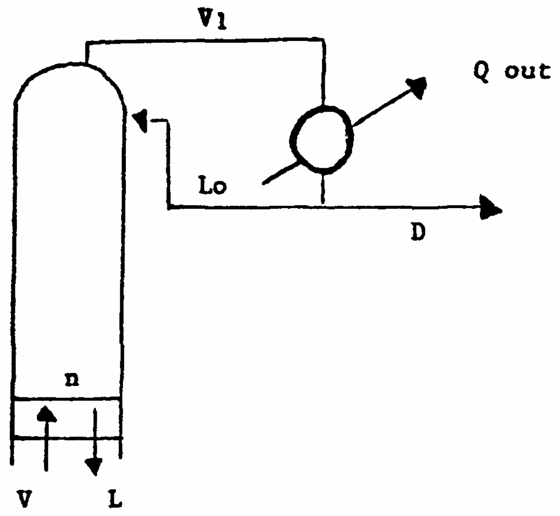


Figure 7.17: Tower Enriching Section

Equation 7-45

$$R = \frac{L}{D}$$

For component A:

Equation 7-46

$$V\,y_{n+1} = L\,x_n + D\,x_D$$

Divide by V:

Equation 7-47

$$y_{n+1} = \frac{L}{V}x_n + \frac{D}{V}x_D$$

Equation 7-48

$$y_{n+1} = \frac{L}{D(R+1)}x_n + \frac{D}{D(R+1)}x_D$$

Or we can say:

Equation 7-49

$$y_{n+1} = \frac{R}{R+1}x_n + \frac{x_D}{R+1}$$

This gives a line with a slope of $\frac{L}{V} = \frac{R}{R+1}$ which intersects the point $X_D\ y_1$. We draw this line on the plot, Figure 7.19. We can also do a material balance around the bottoms section.

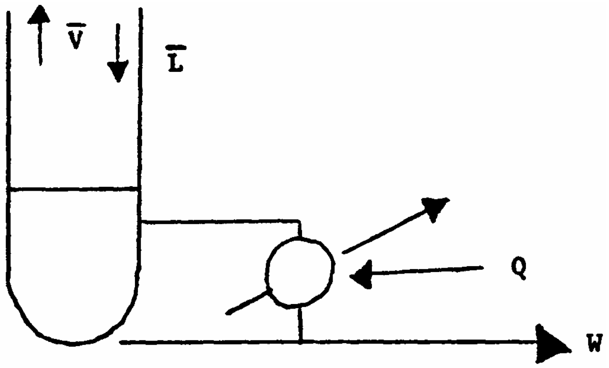


Figure 7.18: Tower Fractionation Section

We find that the operating line will be a line with a slope of

Equation 7-50

$$\frac{\bar{L}}{\bar{V}} = \frac{\bar{L}}{\bar{L} - W}$$

which passes through X_W which is on the 45° line of $y = x$. As yet, however, we have not determined the value of $\bar{L}$. This depends on the condition of the feed.

The condition of the feed sets the $\bar{L}$ so we work on feed instead. First of all we know the composition of the feed Z_F. We set this value on the 45° line (where $y = Z_F$, when $x = Z_F$).

Next we determine a factor "q". "q" is defined by the equation:

Equation 7-51

$$q = \frac{\bar{L} - L}{F} = \frac{H_V - H_F}{H_V - H_L}$$

This is proved by enthalpy balance on the feed plate where H_V is the heat content of a saturated vapour of the composition of the feed. H_L is the heat content of a saturated liquid of the composition of the feed. H_F is the actual heat content of feed.

Now a q line for the feed can be established in which the

slope is:

Equation 7-52

$$\frac{q}{q-1}$$

and it starts at z_F.

Actually on the feed tray it can be shown that

Equation 7-53

$$y = \frac{q\,x}{q-1} - \frac{z_F}{q-1}$$

where:

z_F = composition of the feed.

Now if we have a saturated vapour feed then the line is horizontal:

Equation 7-54

$$\frac{q}{q-1} = 0$$

or if a saturated liquid, the line is vertical:

Equation 7-55

$$\frac{q}{q-1} = \infty = \frac{1}{0}$$

We can determine q from the properties of the components and thus draw the q line.

From the intersection of the q line and the rectifying operating line we can join a line to X_W. This has the slope

$$\frac{\overline{L}}{\overline{L} - W}$$

and is the stripping section operating line. These two lines are drawn on Figure 7.19. We are now ready to find the number of theoretical plates.

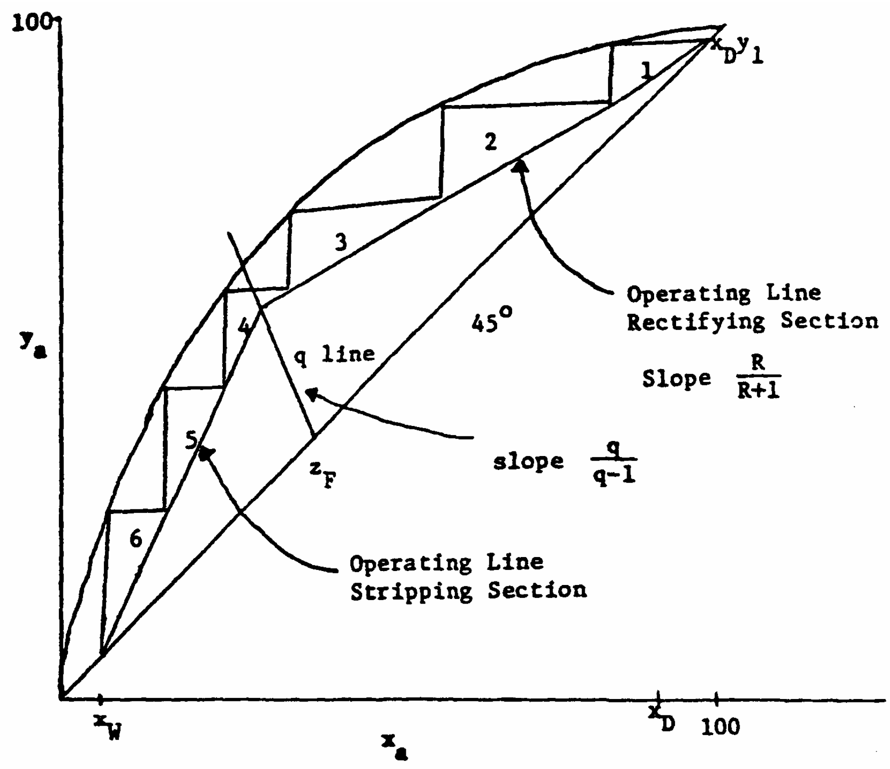


Figure 7.19: McCabe Thiele Diagram

From a known $X_D y_1$ we find x_1 on the equilibrium curve by going horizontally to the equilibriums curve, we find x_1 in equilibrium with y_1. We then drop down to the operating line to find the point $x_1 y_2$ and continue this way until x_w is reached. Then the number of theoretical trays is found by counting the number of horizontal lines.

There are some refinements, like feed tray location, that can be worked out. See Page 539 in Katz[5] for this method.

7.9.4 Ponchon[8] – Savarit[9] Method for Number of Ideal Stages Use of H - X Diagram

The assumption of constant molal latent heat and constant molal overflow in the analysis of fractionating columns is not true for most practical cases. This limitation, and also the simplifying assumption of zero heat of solution of liquids and vapours, may be removed if the analysis is based on enthalpy balances as well as material balance and equilibrium considerations. The method was first proposed by Ponchon and Savaritt.

Binary vapour-liquid equilibrium can be plotted on coordinates of enthalpy vs concentration (at constant P). The liquid solution enthalpies include both sensible heat and the heat of mixing of components:

Equation 7-56

$$H_L = C_{PL}\left(t_L - t_0\right)M_{av} + D_S$$

where:

H_L is liquid enthalpy

C_{PL} is specific heat

t_L is liquid temperature

t_0 is reference temperature

M_{av} is average mole weight

DH_S is heat of mixing.

A typical H-xy diagram is shown in Figure 7.20. The Ponchon - Savarit method represents a graphical solution of the equations of SOREL (material and energy balance equations for each plate). The method of analysis is based on the graphical addition and subtraction of the properties of streams of liquid and vapour streams by the LEVER - ARM rule.

A typical H-xy diagram is shown below where xy are the concentration of the liquid and vapour phases respectively.

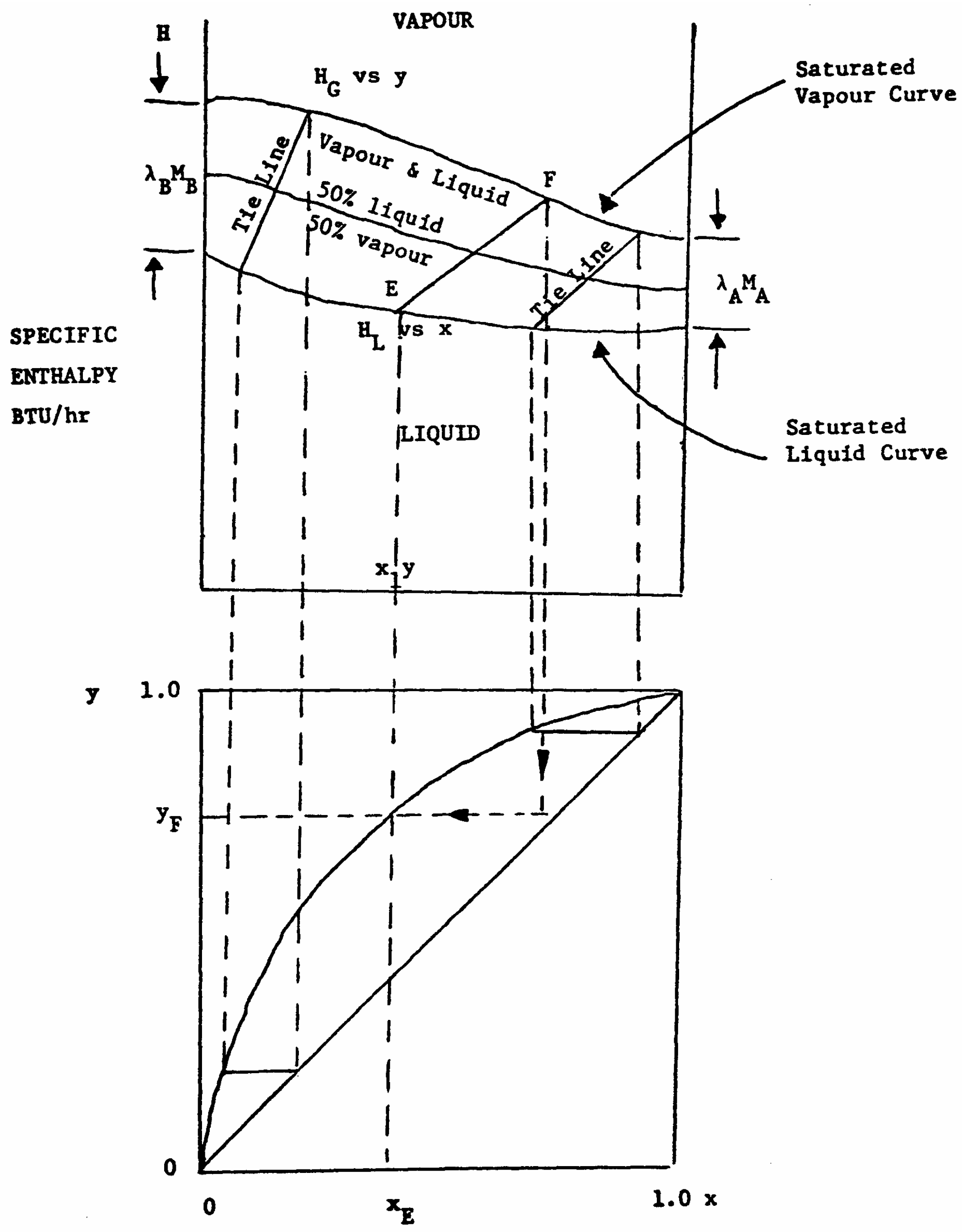


Figure 7.20: Ponchon - Savarit Diagrams

A brief description of the LEVER - ARM rule is given below.

Consider a system as shown in Figure 7.21 in which a binary mixture is fed into a column under such condition that it forms an equilibrium mixture of vapour and liquid. The flow rates will be designated as F (feed), D (distillate) and W (bottoms).

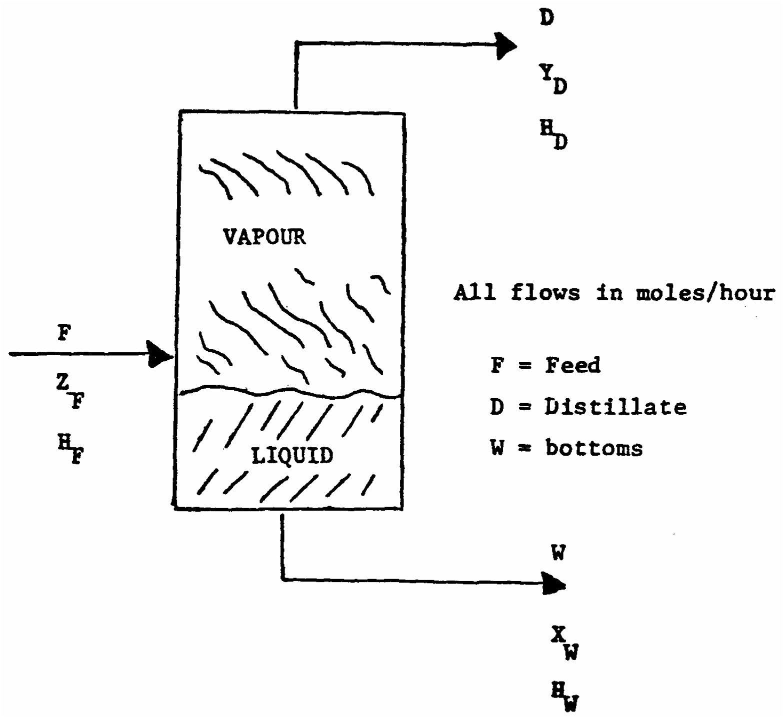


Figure 7.21: Vapour Liquid Program

An overall material balance and a component material balance (for the more volatile component) can be written as follows:

Equation 7-57

$$F = D + W$$

Equation 7-58

$$F\,z_F = D\,y_D + W\,x_w$$

Substituting for F from equation (57) and rearranging (58) we obtain:

Equation 7-59

$$\frac{D}{W} = \frac{z_F - x_w}{y_D - z_F}$$

which provides a relationship between the rates of D and W and the composition of the streams.

We can also write an enthalpy balance for the column:

Equation 7-60

$$F\,H_F = D\,H_D + W\,H_W$$

and again, substituting for F from Equation 57 and rearranging to get

Equation 7-61

$$\frac{D}{W}=\frac{H_F-H_W}{H_D-H_F}$$

By combining equations (59) and (60) we can obtain a relationship between rates, compositions and enthalpies of the streams:

Equation 7-62

$$\frac{D}{W}=\frac{z_F-x_w}{y_D-z_F}=\frac{H_F-H_W}{H_D-H_F}$$

The proportionality between enthalpies and compositions expressed in this equation (60) can also be rearranged to give:

Equation 7-63

$$\frac{1}{slope}=\frac{y_D-z_F}{H_D-H_F}=\frac{z_F-x_w}{H_F-H_W}\quad \text{with a common point } T$$

which indicates that joints W, F and D, on the enthalpy-composition diagram representing feed, distillate and ***bottom streams must be on a straight line***.

Streams D and W are in equilibrium and must be at the ends of a tie line through F.

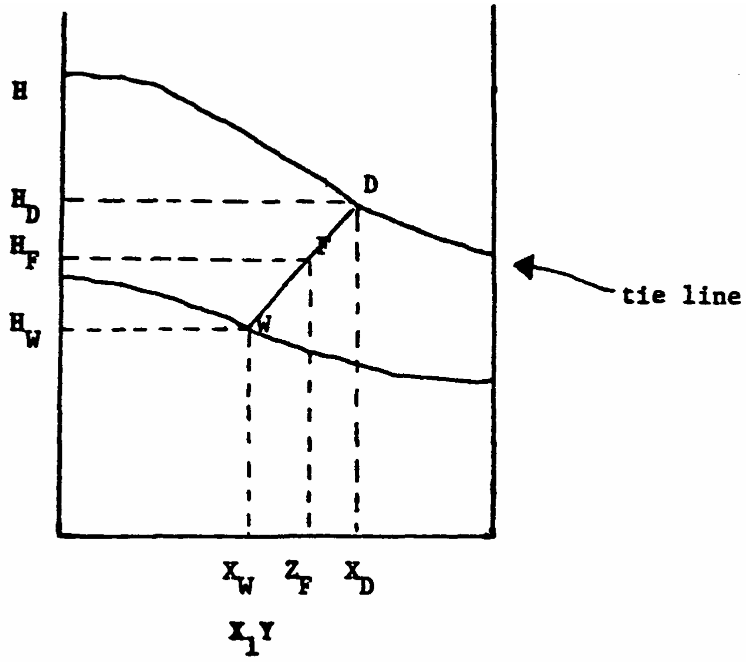


Figure 7.22: More Ponchon - Savarit Diagrams

Equation 7-64

$$\frac{Distillate}{Bottoms}=\frac{\overline{WF}}{FD}$$

Equation 7-65

$$\frac{Bottoms}{Feed} = \frac{\overline{FD}}{WD}$$

and

Equation 7-66

$$\frac{Distillate}{Feed} = \frac{\overline{F}\overline{W}}{WD}$$

7.9.4.1 Analysis of a Fractionating Column

For a column, operating under steady state conditions (shown in Figure7.23), we can write the overall balance, as follows:

From equation 57, F = D + W, and

Equation 7-67

$$F\,z_F = D\,x_D + W\,x_w$$

Equation 7-68

$$F\,H_F + q_r = D\,H_D + W\,H_W + q_c$$

where:

> q_r and q_c are the total heats put into and removed from the reboiler and condenser, respectively.

To represent q_r and q_c on the H-X diagram we can convert them into BTU/lb by noting that

Equation 7-69

$$Q_D = \frac{q_c}{D} \quad BTU/lb\ of\ D$$

Equation 7-70

$$Q_W = \frac{q_r}{W} \quad BTU/lb\ of\ W$$

The overall enthalpy balance can now be written as:

Equation 7-71

$$F\,H_F = D\left(h_D + Q_D\right) + W\left(h_B - Q_W\right)$$

or

Equation 7-72

$$F\,H_F = \Delta_D + \Delta_W$$

where the stream Δ_D has the coordinates (X_D, $h_D + Q_D$) and the stream Δ_W has the coordinates (X_W, $h_W - Q_W$) Equations (71) and (72) can be represented as a straight line (after the method just described) and this is done in Figure 7.24.

All pairs of passing streams within the column can be related to the points which represent Δ_D and Δ_W. The enthalpy balance for the top of the column, for example, is

Equation 7-73

$$V_n H_n = L_{n+1} H_{n+1} + Dh_D + q_c$$

Equation 7-74

$$V_n H_n - L_{n+1} H_{n+1} = D\left(h_D + Q_D\right) = \Delta_D$$

Equation 7-75

$$\frac{V_{n+1}}{D} H_D - \frac{L_0}{D} h_0 = h_0 + Q_D$$

$$V_{n+1} = L_0 + D$$

Equation 7-76

$$\frac{L_0}{D} = \frac{h_0 + Q_D - H_D}{H_D - h_0}$$

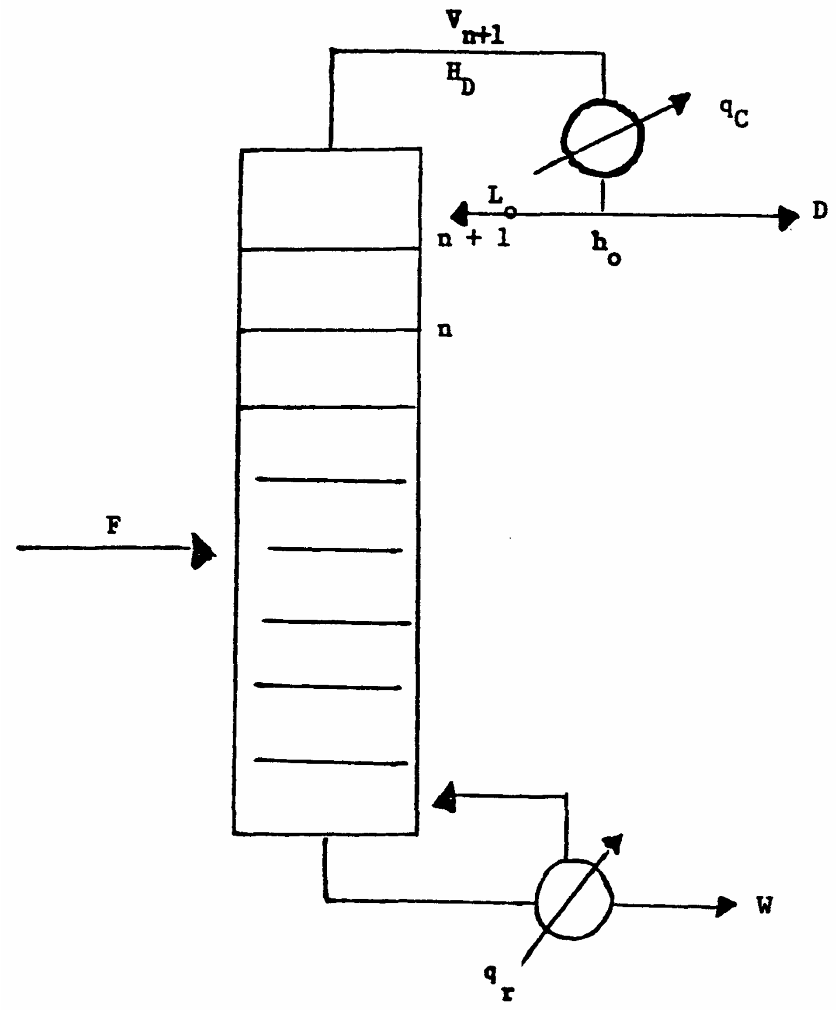


Figure 7.23: PS Tower Analysis Diagram

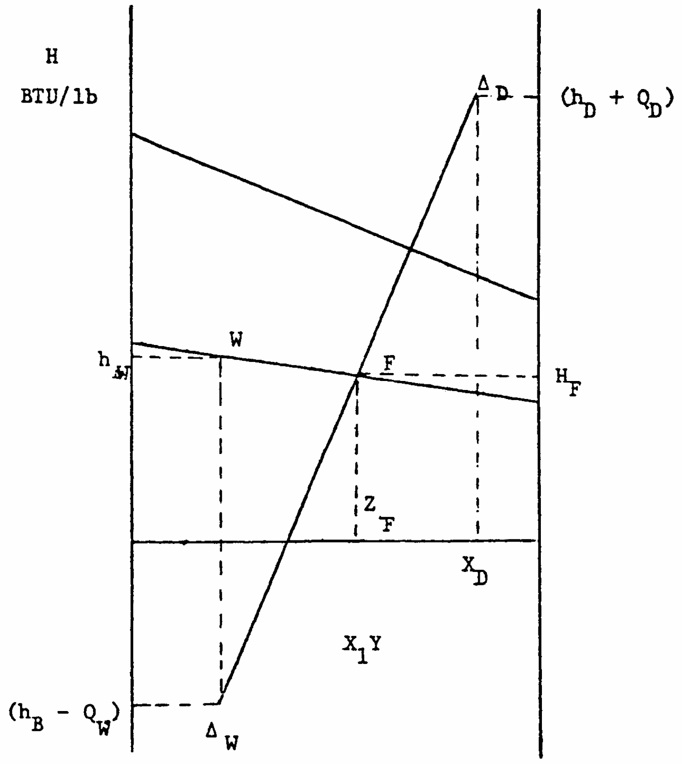


Figure 7.24: Further PS Diagrams

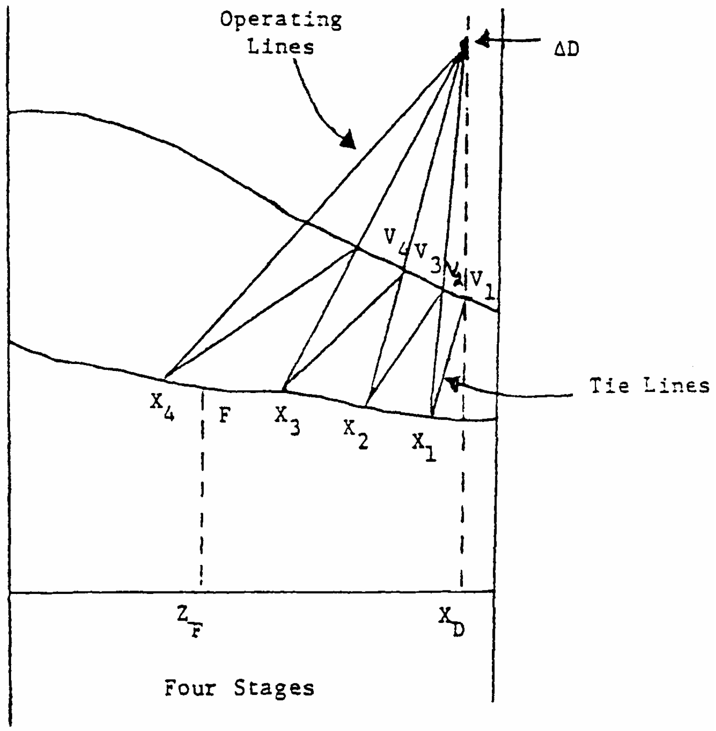


Figure 7.25: Calculation of Number of Theoretical Stages in Rectifying Section

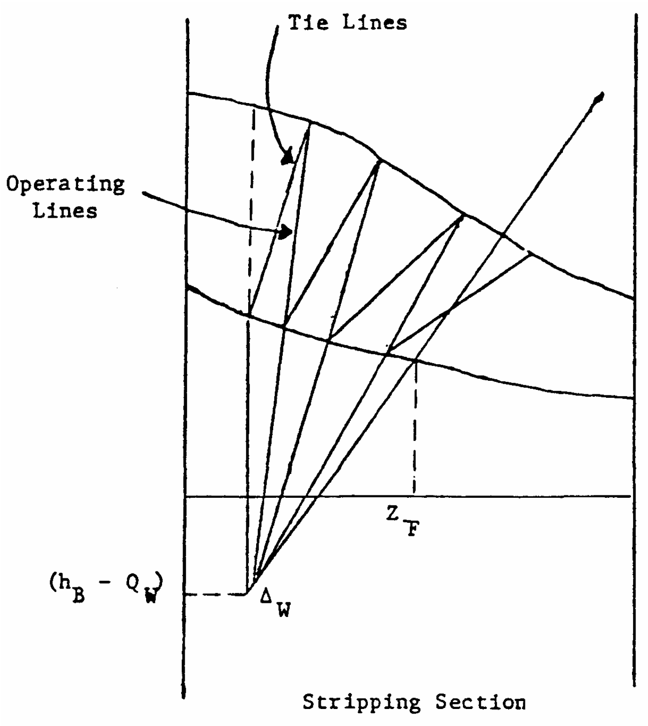


Figure 7.26: Calculation of Number of Trays in Stripping Section

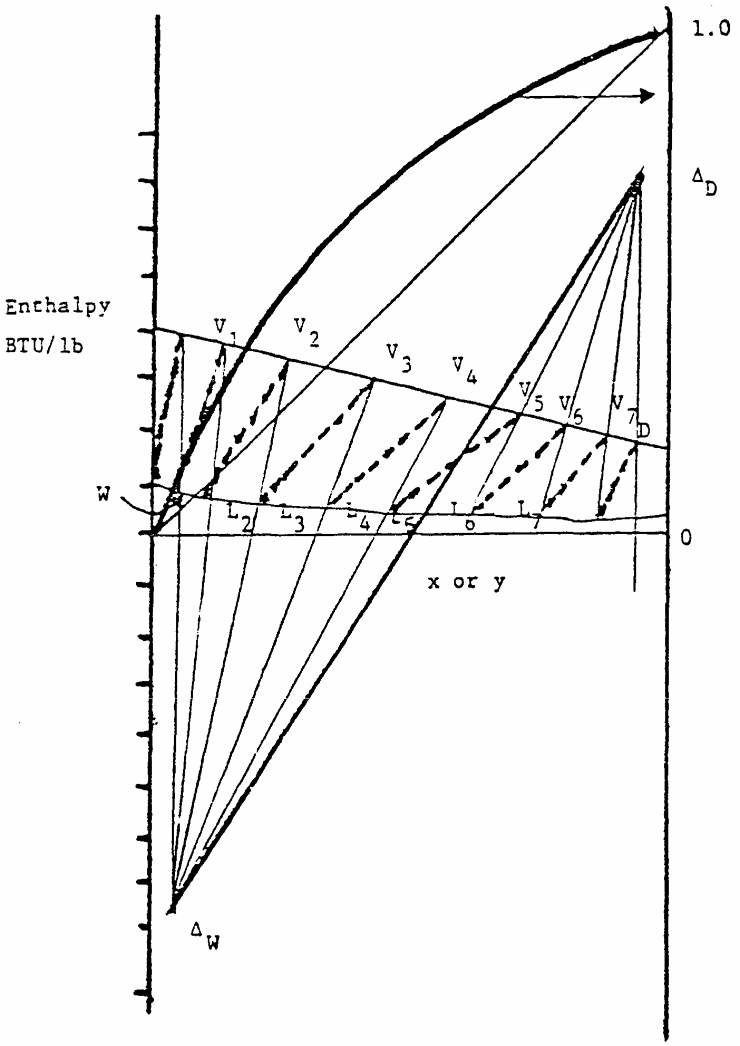


Figure 7.27: Overall Tray Calculation

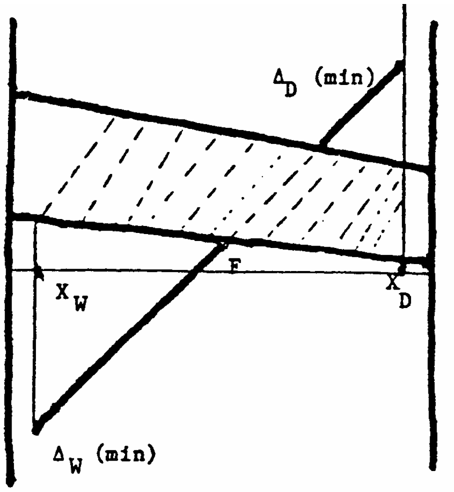


Figure 7.28: Minimum Reflux

Extrapolate the tie line which passes through the feed point F until it intersects the vertical line at X_D.

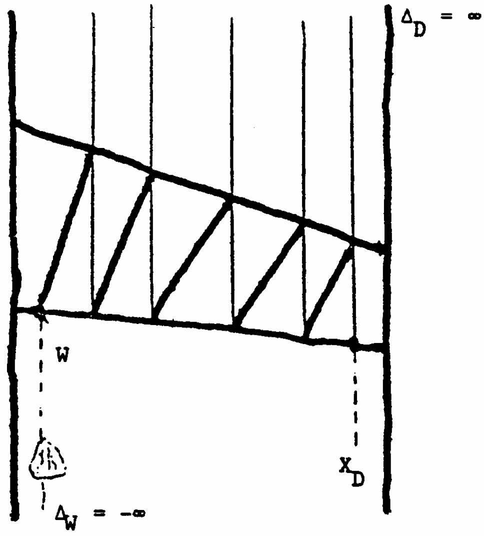


Figure 7.29: Total Reflux

Δ_D is at infinity. Therefore the operating lines are vertical.

7.9.5 Multicomponent Mixtures

The next problem is determining the number of trays for a multicomponent mixture. This is done by quite complex methods. There are a few short cut methods and also some general plate calculations using primary computers. One short cut method is based on the following:

1. Calculate minimum reflux ratio (when we have an infinite number of plates).
2. Calculate minimum number of equilibrium stages (when we have an infinite reflux).
3. Calculate actual number of equilibrium stages from minimum reflux ratio and minimum equilibrium stages using actual reflux.

To determine the minimum reflux and the minimum number of plates one method is to follow that outlined in Maxwell, Page 230.

This is the so-called Fenske Underwood Method. Let us define some quantities.

Key Component - The components that appear in both the top and bottom of fraction tower.

Light Key Component (LK) - The light component; appear primarily in the overhead.

Heavy Key Component (HK) - The heavy component; appear primarily in the bottoms.

α - The relative volatility is the ratio of the K at a specific condition ot temperature and pressure for a component to the K value for the heavy key component.

Subscript LK and HK - mean light and heavy key components.

D - distillate or overhead product as a subscript (mols. dist./100 moles feed)

W - refers to bottom product as subscript and moles/bottom prod./100 moles feed

X - moles of any product/100 moles in distillate or bottoms of feed

x - mole fraction of any component in liquid

L - means any light component

H - means any heavy component exclusive of LK and HK

O - moles reflux/100 moles feed

Now to find the minimum number of plates the Fenske Equation can be used.

Let SM be minimum number of plates:

Equation 7-77

$$\alpha_{LK}^{SM} = \frac{(X_{LKD})(X_{HKW})}{(X_{LKW})(X_{HKD})}$$

Since we have assumed the final product's composition we can find SM. To evaluate α should find α at the top of the tower at dew point of distillate, α at bottom of tower at bubble point of bottoms, take the average tower temperature and pressure, and find α, then multiply all three α's together and take 1/3 of this value. For ease take just arithmetic average of temperature and pressure at top and bottom and use this for finding α.

The next problem is to calculate the minimum reflux. A method of doing this is the Underwood correlation. This is done by the use of two equations:

Equation 7-78

$$\frac{\alpha_1 x_{1F}}{\alpha_1 - \theta} + \frac{\alpha_2 x_{2F}}{\alpha_2 - \theta} + \ldots\ldots + \frac{\alpha_n x_{nF}}{\alpha_n - \theta} = 1 - q$$

Equation 7-79

$$\frac{\alpha_1 x_{1D}}{\alpha_1 - \theta} + \frac{\alpha_2 x_{2D}}{\alpha_2 - \theta} + \ldots\ldots + \frac{\alpha_n x_{nD}}{\alpha_n - \theta} = R_{\min} + 1$$

where

Equation 7-80

q = heat ratio of feed used in McCabe Thiele Method

$$= \frac{H_V - H_F}{H_V - H_L}$$

x_F = composition in feed (mole fraction)

x_D = composition in overhead product (mole fraction)

R_{min} = minimum reflux

θ = a mathematical term but can be estimated from knowing $\alpha_{LK} > \theta > \alpha_{HK}$

The method in general is to find θ. Then knowing θ find R_{min}.

Van Winkle and Todd[18] have developed a graph giving approximate values of θ. Figure 7.30 shows this data.

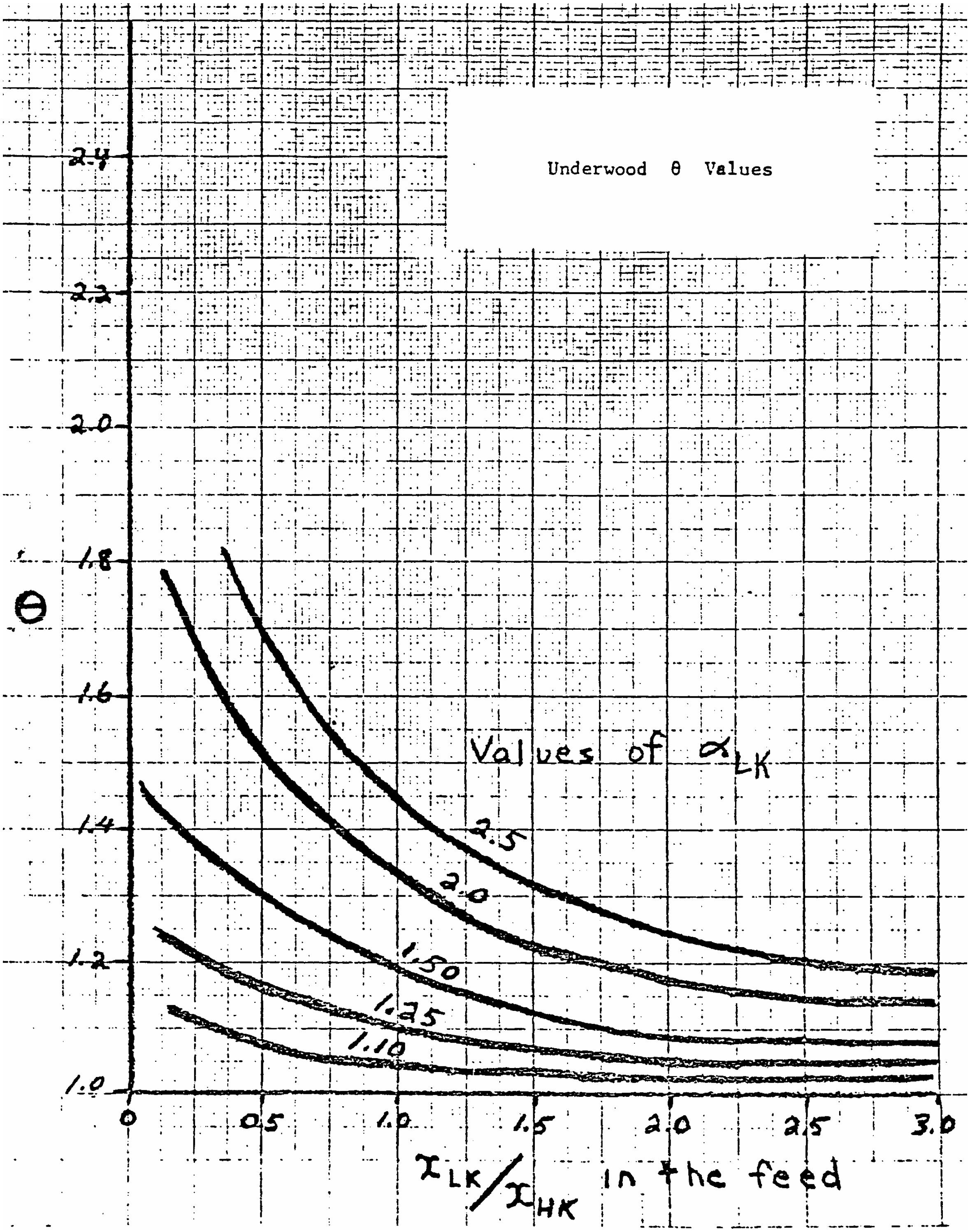


Figure 7.30: Underwood θ Values

Now to find the *actual number of plates* a graph has been prepared by Gilland[12] giving the ratio of Actual Number of theoretical of plates to minimum versus actual reflux to minimum. This is shown as a nomograph and is given as Figure 7.32. It is based on the equation:

Equation 7-81

$$\frac{S - S_{\min}}{S + 1} = f\,\frac{R - R_{\min}}{R + 1}$$

Mapstone , in Hydrocarbon Processing, Page 169, May 1968, developed this nomograph.

The next item in the method is to pick an actual reflux. An actual reflux is an economic balance between tower height (low reflux compared to minimum, thus giving a high number of trays), and the tower diameter (high reflux and thus high through-put). Here are some values that are commonly used:

Table 7.4: Common Reflux Values

	O/D Reflux Overhead Product	Reflux to Feed
Deethanizer	----	0.5-1.0
Depropanizers	4-6	1.0-2.0
Debutanizer	2-3	0.6-2.0
Butane Splitters	10-12	4.0-5.0
Stabilizer	2-3	0.5-2.0
Pentane Splitters	10-12	4.0-5.0

Note: Typical application is 1.2 x minimum for an economic reflux rate.

For special columns an actual economic analysis should be run. The figure below shows the type of results that will be obtained:

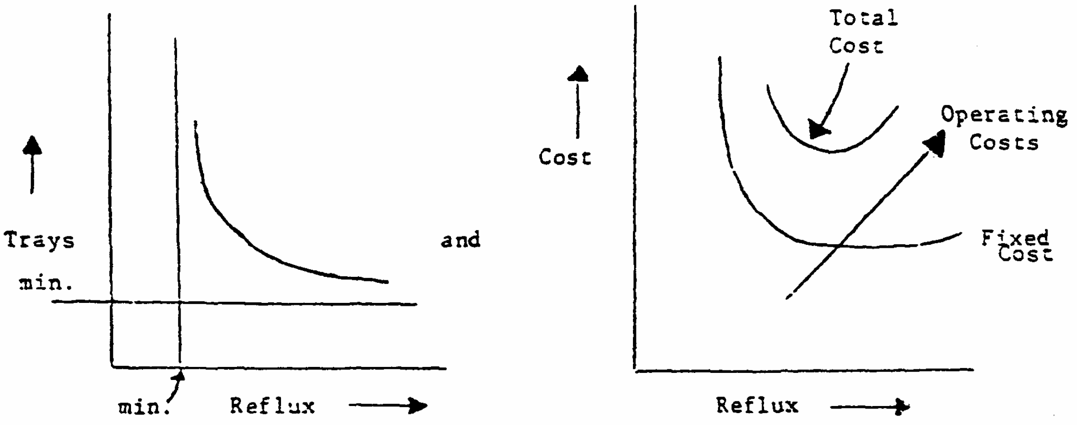


Figure 7.31: Economics of Number of Trays

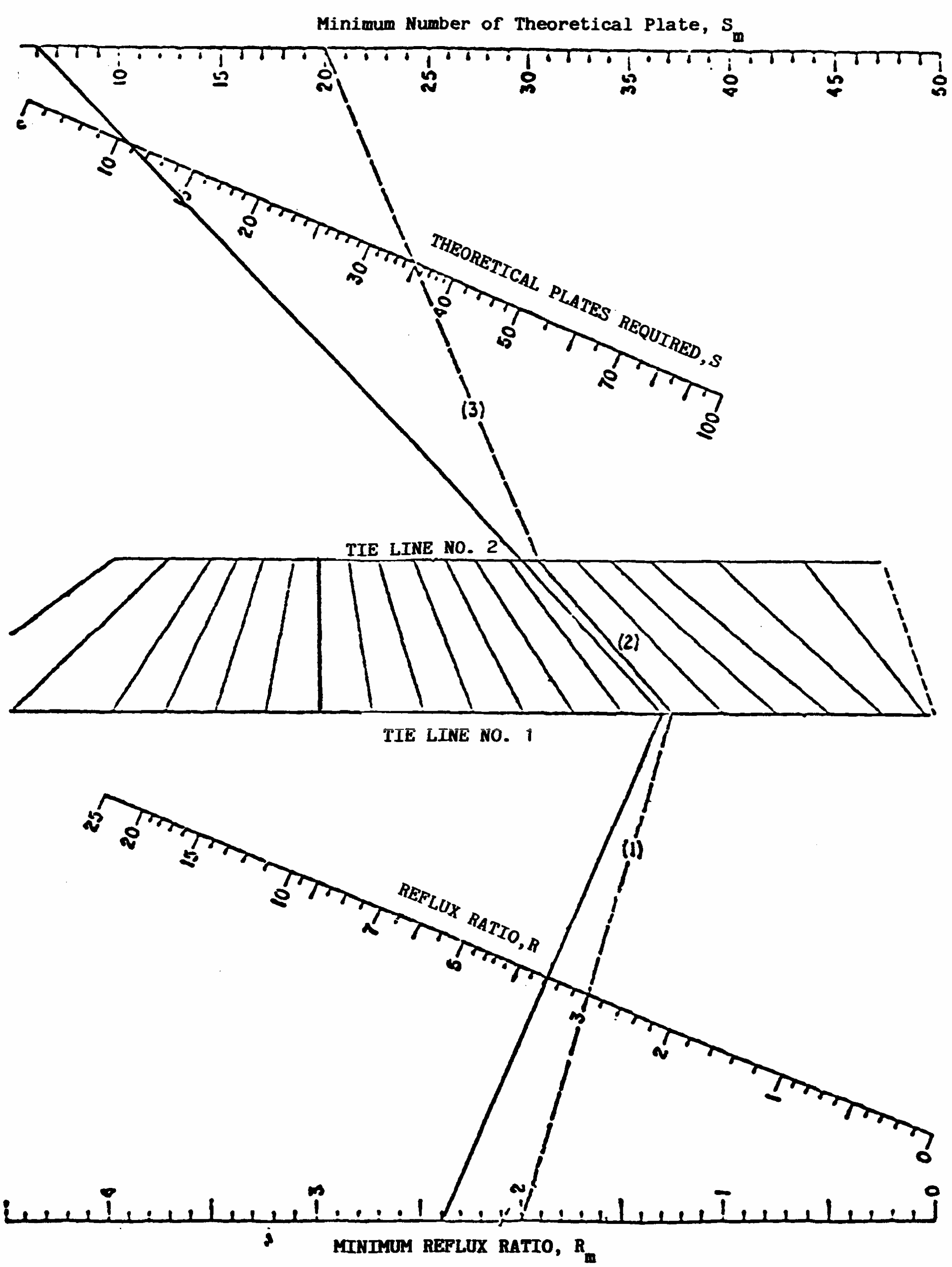


Figure 7.32: Gilliland's Calculation for the Number of Theoretical Plates

Example Problem 7.1

Determine the number of theoretical trays required for depropanizing a feed of the composition given below. The tower is to operate at 300 psig. The top temperature is 100°F and the bottom temperature is 310°F. The anticipated separation is also given in the table below. The minimum reflux ratio for the separation is 2.0 (O/D) and the operating reflux ratio is expected to be approximately twice the minimum.

Comp.	Feed Composition Mole %	Overhead Product Moles/100 moles feed	Bottoms Product Moles/100 moles feed
C_l	5.1	5.1	
C_2	8.8	8.8	
C_3	21.0	20.5	0.5
iC_4	7.0	0.3	6.7
nC_4	13.0		13.0
iC_5	7.2		7.2
nC_5	12.4		12.4
C_6	25.5		25.5

The method of Fenske will be used.

Find α_{LK} - For simplification, we will take it at 300 psig and 205°F.

Equation 7-82

$$\alpha_{LK} = \frac{KC_3}{KiC_4}$$

Use NGPSA "K" data and assume P_K = 2000

Equation 7-83

$$\alpha_{LK} = \frac{1.6}{0.92} = 1.74$$

Now the Fenske equation:

Equation 7-84

$$\alpha_{LK}^{SM} = \frac{(X_{LKD})(X_{HKW})}{(X_{LKW})(X_{HKD})}$$

Equation 7-85

$$(1.74)^{SM} = \frac{(20.5)(6.7)}{(0.5)(0.3)} = 925 \qquad so\ SM = 12.3$$

Now from Figure 7.32, since we know minimum number of trays, minimum reflux and actual reflux, the theoretical number of trays = 18. The actual required number of trays is determined by subtracting 1 from the ideal number of trays to take care of the reboiler and dividing the remaining number by the tray efficiency.

The location of the feed plate is also quite a detailed calculation. Here is a well known formula for locating the feed tray:

Equation 7-86

$$\log_{10}\left(\frac{Plates\ above\ feed}{Plates\ below\ feed}\right) = 0.206\log_{10}\left[\left(\frac{W}{D}\right)\left(\frac{Z_{HK}}{Z_{LK}}\right)\left(\frac{X_{LKW}}{X_{HLD}}\right)^2\right]$$

It should be noted that most actual towers have 3 feed nozzles.

7.9.6 Efficiency

We have determined the number of theoretical plates or equilibrium required for a separation. The next problem is the number or actual plates required. This is determined by dividing the tray efficiency into the theoretical number of trays.

$$E\left(overall\ efficiency\right) = \frac{n^* \left(number\ of\ theoretical\ trays\right)}{n\left(number\ of\ actual\ trays\right)}$$

The tray efficiency can be correlated against α of key comp. X μ, viscosity of feed.

Another method is to use the correlation of density and of flood as developed by Koch Engineering and shown as Figure 7.33. This also applies only to Fractionators.

For a rough guide use E for fractionator	~ 75%
absorbers	35% for C_5 as key components.
	30% for C_4 as key components.
	25% for C_3 as key components.

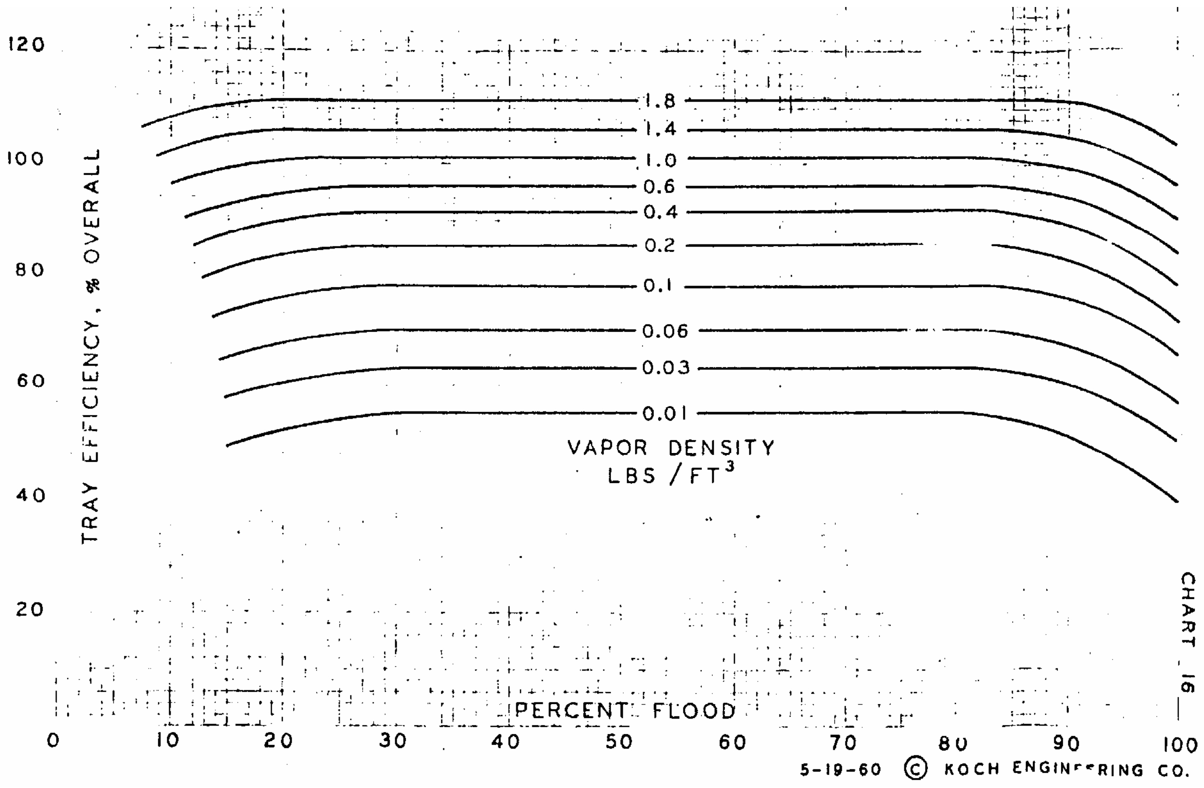


Figure 7.33: Efficiency Correlation

7.10 Tower Height Absorption

7.10.1 General

Let us consider what happens in a tower when absorption takes place. Consider first a two component system in both gas and liquid phases. In gas, assume pure gas with solute and in liquid assume pure solvent and solute. If we allow gas phase and liquid to come together they will eventually reach equilibrium. Thus we can, for fixed temperature and pressure conditions, get an equilibrium curve showing the relation between the concentration of the solute in the gas phase and in the liquid phase.

For example, here are some curves for NH_3 in air and water:

Solute - material being absorbed

Solvent - carrier fluid

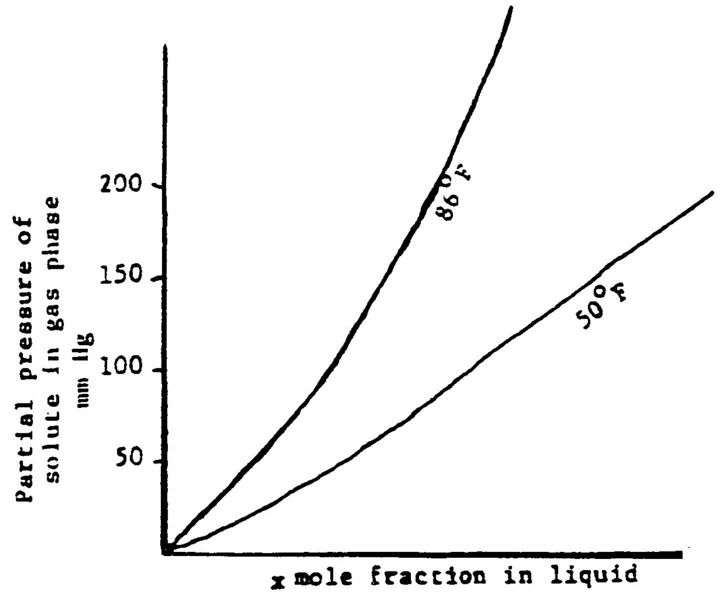


Figure 7.34: Absorption Curves

These curves can sometimes be expressed by:

4. Raoult's Law (when have ideal solution and gas)

Equation 7-87

$$P_v = P_{vp}\, x$$

where:

P_v = partial pressure of solute in the gas

x = mole fraction of the solute in solvent.

P_{vp} = vapour press.

5. Henry's Law. This law is more often applicable.

Equation 7-88

$$P_v = m' x$$

where:

m' = Henry's Law constant.

Note: Henry's Law constant is determined experimentally. It is generally applied to dilute solutions.

7.10.2 Absorption of a Single Component

As in distillation we can apply a graphical method for solving the number of theoretical plates required in an absorber absorbing one component from an inert carrier gas and with a non-volatile solvent. We plot an equilibrium curve with ordinates of:

$$Y = \frac{moles\ \ solute}{moles\ \ inert\ \ carrier\ \ gas} \qquad and \qquad X = \frac{moles\ \ solute}{moles\ \ inert\ \ solvent\ \ in\ \ liquid}$$

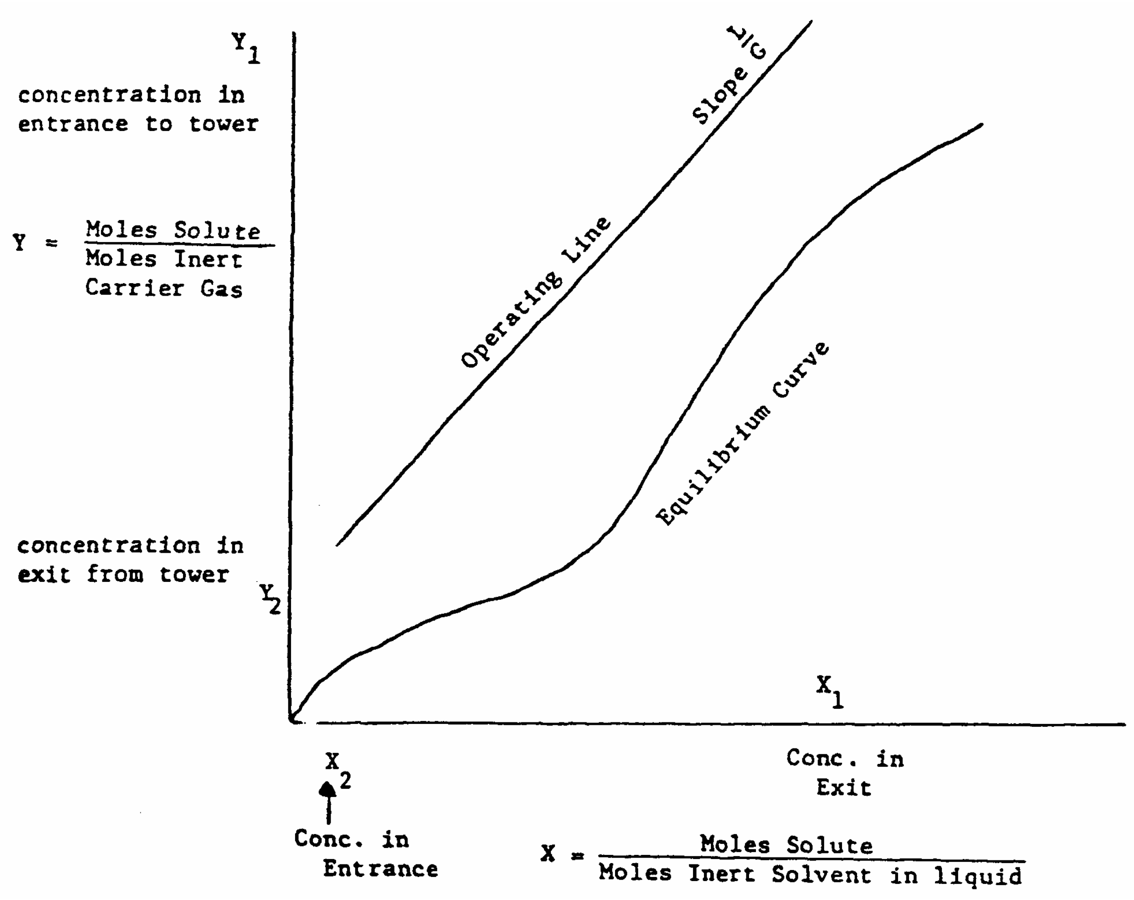


Figure 7.35: More Absorption Curves

Figure 7.36 shows the tower to which Figure 7.35 refers. Let us consider a counter current absorber.

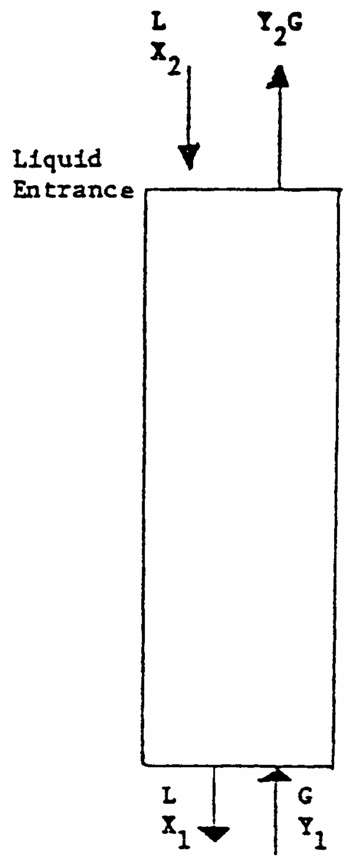


Figure 7.36: Counter Current Absorber

where:

G = moles/hr/sq.ft. of insoluble carrier gas.

L = moles/hr/sq.ft. of inert liquid.

A material balance can be written to show that the operating curve of slope $\frac{L}{G}$ passes through X_1,Y_1 and X_2,Y_2 . Thus the number of trays can be stepped off. A stripper operates with operating curve below equilibrium line.

7.10.3 Multicomponent Absorption

For multicomponent absorption problems we need to introduce the absorption factor concept. This was developed by Kremser and modified by Brown and others. Consider the material balance around an abosrber plate "i" as shown in Figure 7.37 in a "n" number trays absorber.

Note: The absorption calculations as contrasted to some distillation calculations, the trays are numbered from top to bottom.

Equation 7-89

$$L_0\left(X_i - X_{i-1}\right) = V_{n+1}\left(Y_{i+1} - Y_i\right)$$

where:

L_O = moles of lean oil entering the absorber.

V_{n+1} = moles rich gas entering absorber.

X_i = mole of single comp. in liquid leaving plate i.

X_{i-1}= moles of single comp. in liquid to plate i per mole of lean oil.

Y_i = moles of single comp. in gas from plate i per mole of rich gas.

Y_{i+1} = moles of single comp. in gas to plate i per mole of rich gas.

Note: X is mole ratio and x is mole fraction.

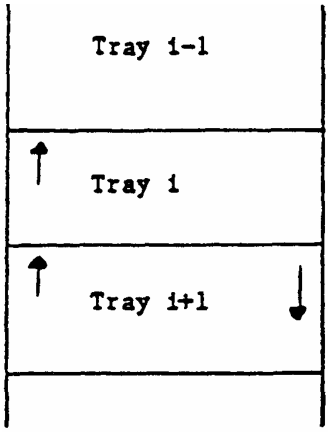


Figure 7.37: Tray Numbering in Absorption

The actual mole fractions of vapour and liquid are

Equation 7-90

$$y_i = \frac{Y_i\left(V_{n+1}\right)}{V_i}$$

Equation 7-91

$$x_i = \frac{X_i\,L_0}{L_i}$$

where:

V_i = mole of gas leaving plate "i".

L_i = moles of liquid leaving plate "i".

y_i = mole fraction of comp. in gas leaving "i'.

x_i = mole fraction of comp. in liquid leaving "i".

Equation 7-92

$$y_i = K_i\,x_i$$

and

Equation 7-93

$$Y_{i-1} = K_{i-1}\, x_{i-1}$$

K_i and K_{i-1} are the equilibrium constants for a single component or tray i and i-1 respectively. Substitute

Equation 7-94

$$Y_i = K_i \frac{L_0}{L_i} \frac{V_i}{V_{n+1}} X_i$$

also

Equation 7-95

$$Y_{i-1} = K_{i-1} \frac{L_0}{L_{i-1}} \frac{V_i}{V_{n+1}} X_{i-1}$$

Now substitute in (89) for X_i and for X_{i-1} in terms of Y and find Y_i.

Equation 7-96

$$Y_i = \frac{Y_{i+1} + \dfrac{L_{i-1}}{K_{i-1} V_{i-1}} Y_{i-1}}{L + \dfrac{L_i}{K_i V_i}}$$

Equation 7-97

$$Let \quad A = \frac{L}{KV} \quad or \quad A_i = \frac{L_i}{K_i V_i} \quad or \quad A_{i-1} = \frac{L_{i-1}}{K_{i-1} V_{i-1}}$$

We have

Equation 7-98

$$Y_i = \frac{Y_{i+1} + A_{i-1} Y_{i-1}}{L + A_i}$$

We can eventually expand this equation to the following if we assume A is constant through tower.

Equation 7-99

$$Absorption\ \% = \frac{Y_{n+1} - Y_1}{Y_{n+1} - Y_0} = \frac{A^{n+1} - A_0}{A^{n+1} - 1}$$

Note: The left hand of the equation above is the amount of a single component absorbed.

where:

n = the number of theoretical stages.

Y_O = moles of a single comp. in gas in equilibrium with lean oil per mole of entering gas, i.e. with 100% stripped lean oil, "Y_O" = 0.

Y_{n+1} = moles of single comp. in rich gas entering column/mole of rich gas.

Y_1 = moles of a single comp. in gas leaving top plate/mole of rich gas.

A chart of absorption factors "A" where "A" versus

Equation 7-100

$$\frac{Y_{n+1} - Y_1}{Y_{n+1} - Y_0}$$

versus number of plates is given on Figure 15-51 of GPSA Data Book.

This assumes that "A" is constant through the tower which is not necessarily so because $\frac{L}{V}$ changes and the temperature affects K.

Let us next consider a stripping column as shown.

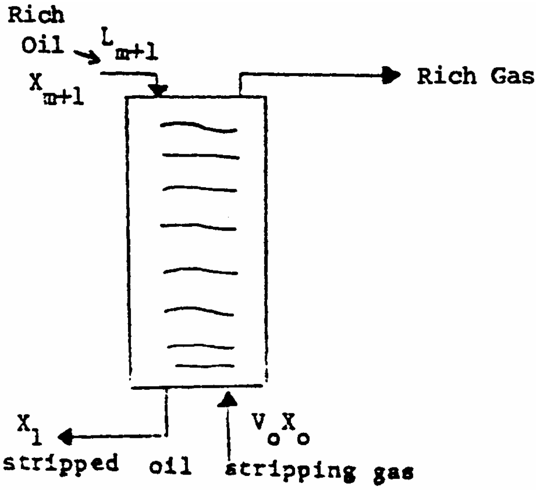


Figure 7.38: Stripper Operation

We can also write a similar equation for stripping:

Equation 7-101

$$\frac{X_{m+1} - X_1}{X_{m+1} - X_0} = \frac{S^{m+1} - S}{S^{m+1} - 1}$$

where:

X_1 = moles of comp. in stripped lean oil leaving stripper per mole of rich oil.

X_{m+1} = moles of comp. in rich oil entering stripper per mole of rich oil.

X_O = moles of comp. in liquid in equilibrium with stripping medium per mole of rich oil.

m = number of theoretical stripping trays.

S = stripping factor $\frac{KV}{L}$.

Same chart as used for the absorption factor can be used for stripping.

7.10.4 Simplified Method for Finding the Number of Trays for Absorption (Short Cut Method)

Given the gas rate, the oil rate and the % absorption of the key component

1. Calculate from rich gas rate and lean oil rate.
2. From operating temperature and pressure find K for key component and thus calculate $\frac{L}{VK}$.
3. Go to chart Figure 15-50 in GPSA Data book and read the number of theoretical trays required for the desired key component recovery.
4. This gives a very conservative value (a larger number of trays than probably required), thus it is probably better to use one of the methods discussed further on.

7.10.5 Kremser Brown Method of Finding the Number of Trays for Absorption

Let us consider the Kremser Brown method of finding the number of trays for a specific absorption.

Given the gas rate, the oil rate and % absorption of the key component.

1. Calculate $\frac{L}{V}$ from rich oil rate (have to estimate amount of liquid absorbed) and rich gas rate.
2. From operating temperature and pressure find K for the key component and thus calculate $A = \frac{L}{KV}$ (Key comp. one being absorbed).
3. Go to chart Figure 15-51 in GPSA Data Book and read the number of theoretical trays required for the desired key component recovery.
4. Calculate % recovery of other components for this number of trays and the same $\frac{L}{V}$ ratio but a different K value because of a different component.
5. Check to see that L assumed is OK - as long as it is not too much lower than that assume that it is probably OK to use.

7.10.6 More exact methods for finding absorption factors

7.10.6.1 Horton & Franklin Method

Find effective plate and use conditions there. Find effective plate "i" from value of A for key absorption component, i.e. one that is being absorbed 50 to 80% (mostly C_3).

Value of "A"	Ratio $\frac{i}{n}$
0.0 - 0.1	1.0
0.1 - 0.4	0.9
0.4 - 1.0	0.8
1.0 - 4.0	0.7
4.0 - ---	0.6

Find V_i from equation

Equation 7-102

$$V_i = V_1 \frac{n+1-i}{n}$$

Equation 7-103

$$\frac{V_i}{V_{i+1}} = \frac{V_1^{1/n}}{V_{n+1}}$$

By material balance find

$$L_i = L_0 + V_{i+1} - V_1$$

We find the temperature by use of the following equation

Equation 7-104

$$\frac{T_n - T_i}{T_n - T_0} = \frac{V_{n+1} - V_{i+1}}{V_{n+1} - V_1}$$

Thus we have V_i, L_i and Temperature, and thus find “A”.

7.10.6.2 Edmister Method

The Edmister[17] method uses an absorption factor based primarily equation

Equation 7-105

$$A_e = \sqrt{A_n\left(A_1+1\right)+0.25} - 0.5$$

where:

A_e = effective absorption factor.

n = leaving nth plate (bottom of tower conditions).

1 = entering 1st plate (top of tower conditions).

7.10.7 Encountered Problems

Let us consider some of the problems in using a constant "A" or "S". A graph is given in Katz telling the maximum temperature rise against lbs. of gas absorbed/lb. solvent, on page 519.

7.10.7.1 Temperature Effects

A typical temperature profile in an absorber is shown in Figure 7.39. As can be seen the temperature in the tower varies a great deal.

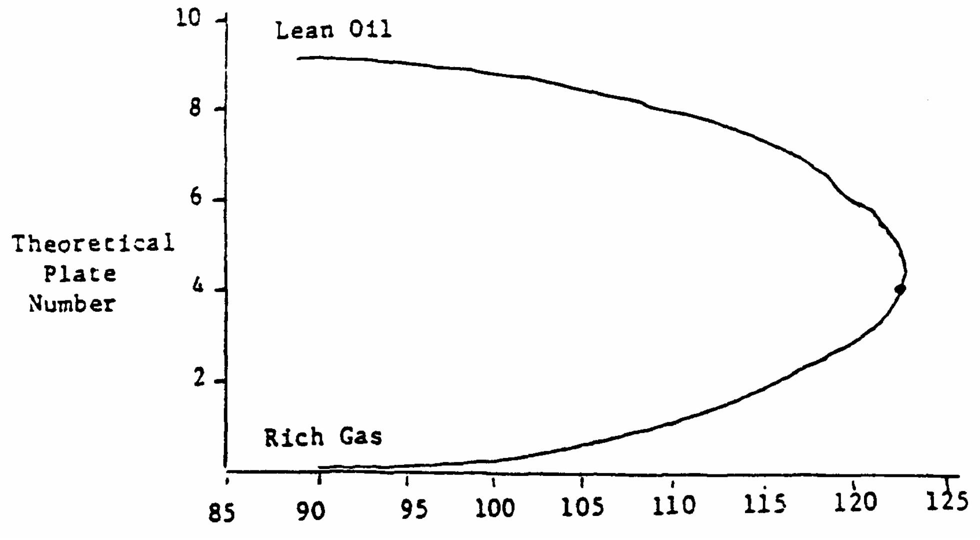


Figure 7.39: Temperature of Absorption

7.10.7.2 Changes Throughout the Tower

$\frac{L}{V}$ changes throughout the tower. The moles of liquid increase as material is absorbed throughout the tower and the moles of rich gas obviously decrease.

Example Problem 7.2

Calculate the number of theoretical plates required to absorb 80% of the propane in the gas of the composition given in the table below. The gas flow is 50 MMSCFD to the tower and the lean oil rate is 200 US gpm of a 140 mole wt. oil with a gravity of 50° API. The tower operates at 900 psig and 0°F.

f) Simplified or Shortcut method.

Find:

$$A = \frac{L}{VK}$$

$$\text{V} = \text{Rich} = \frac{50\,x\,10^6}{379} = 132{,}000\ moles/day$$

$$\text{L} = \text{Lean Oil} = \frac{200\,(8.33)\,(.7796)\,(60)\,(24)}{140} = 13{,}400\ moles/day$$

K_{C_3} at 900 psig and 0°F = 0.13

$$A = \frac{L}{VK} = \frac{13.400}{132{,}000(.13)} = .78$$

Number of trays required = 9

g) Use Edmister's Method.

Gas Analysis:

Comp.	**Mole %**	K^0_{900} **psig ***	**Estimate of % Absorption ♠**	**Moles/100 moles Feed Absorber**
N_2	0.30	9.4	nil	0.00
C_1	91.63	2.6	3.9	3.57
C_2	5.72	0.48	21.1	1.21
C_3	1.63	0.13	80 (given)	1.30
iC_4	0.29	0.052	97	0.28
nC_4	0.31	0.037	100	0.31
C_5	0.12	0.016	100	0.12
			Total	**6.79**

* - Using P_K = 5000 and NGSMA (1957) K's

♠ - Estimated by calculating $\frac{L}{VK}$ for each component and using 9 theoretical trays.

Find A_1 and A_n

V for A_n = $V_{\text{Rich Gas}}$ 132,000 moles/day

$L_n = L_{\text{Rich Liquid}} = L_{\text{Lean Oil}} + L_{\text{Liquids Absorbed}}$

$L_{\text{Liquids Absorbed}}$ = 0679 (132,000) = 8963 moles/day

L_n = 13,400 + 8963 = 22,363 moles/day

$$: A_n = \frac{22{,}363}{132{,}000\,(.13)} = 1.30$$

V and $A_1 = V_{\text{Lean Gas}}$ = 132,000 - 8,963 = 123,067 moles/day

$L_1 = L_{\text{Lean Oil}}$ = 13,400

$$: A_1 = \frac{13{,}400}{123{,}067\,(.13)} = 0.84$$

Find A_e

$$= \sqrt{A_n\,(A_1+1)+.25} - 0.5$$

$$= \sqrt{A_n\,(A_1+1)+.25} - 0.5 = 1.13$$

No. of trays for 80% C_3 absorption = 3.1

7.11 Adsorption

This is the phenomena of mass transfer from a gas to solid (or liquid to solid). Such operations as drying or leaching are the reverse of this.

We will consider only gas adsorption. There are two types.

7.11.1 Physical Adsorption (van der Waal's Adsorption)

In this there is inter-molecular attraction between the molecules of the adsorbent (material which is adsorbing) and absorbate (material which is being adsorbed). Quite often the inter-molecular force is greater than the force between the gas itself and it condenses on the adsorbent even though the vapour pressure of the condensate is greater than pressure of the substance in the gas at this temperature. Heats of adsorption in this case are similar to heats of sublimation. This phenomena is reversible.

This type of adsorption can be described by the so-called Freundlich Equation

Equation 7-106

$$w_i = \alpha\left(p_i\right)^n$$

where:

w = the concentration of adsorbate on adsorbent lb/lb

ρ_i = partial pressure of adsorbate

α = constant

n = constant

7.11.2 Chemical Adsorption

In this case a chemical reaction takes place and if chemical bond is strong the process is not easily reversible.

7.11.2.1 Equilibrium Data

As in other mass transfer operations we have experimental equilibrium data. We actually obtain equilibrium of material in a gas phase versus percent adsorbed on bed. A typical adsorption equilibrium curve is shown below

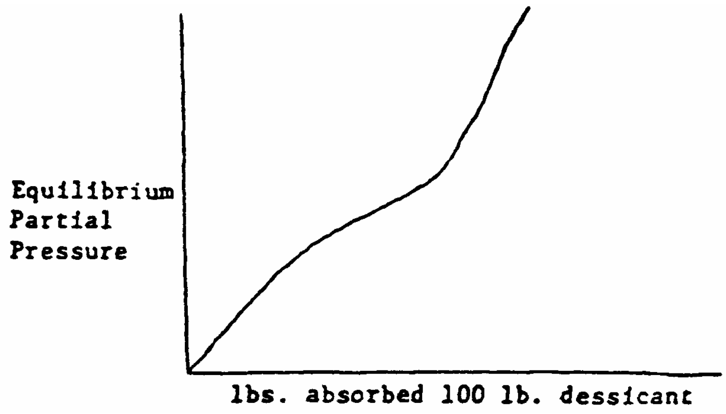


Figure 7.40: Adsorption Curve

7.11.3 Nature of Adsorbents

These are usually granular in form. In particular they are characterized by having an extensive internal surface, i.e. a lot of internal pores. For example, gas mask charcoal has 1,000,000 sp. meters of surface per Kilogram of substance.

7.11.4 How Adsorption Proceeds

We are mostly concerned with the adsorption of H_20 and HC and how facilities for doing this job are designed. Let us consider how the adsorption of C_3, C_4, C_5^+ proceeds. Figure 7.42 shows this. First of all, water is adsorbed with the heavier hydrocarbons and finally the light ones.

7.11.5 Sizing of Beds

To determine length of bed, need to know volume of adsorbent to use. This can be obtained from dynamic equilibrium curves as shown in Figure 7.41 which shows data for C_4, C_5 and C_6 adsorption.

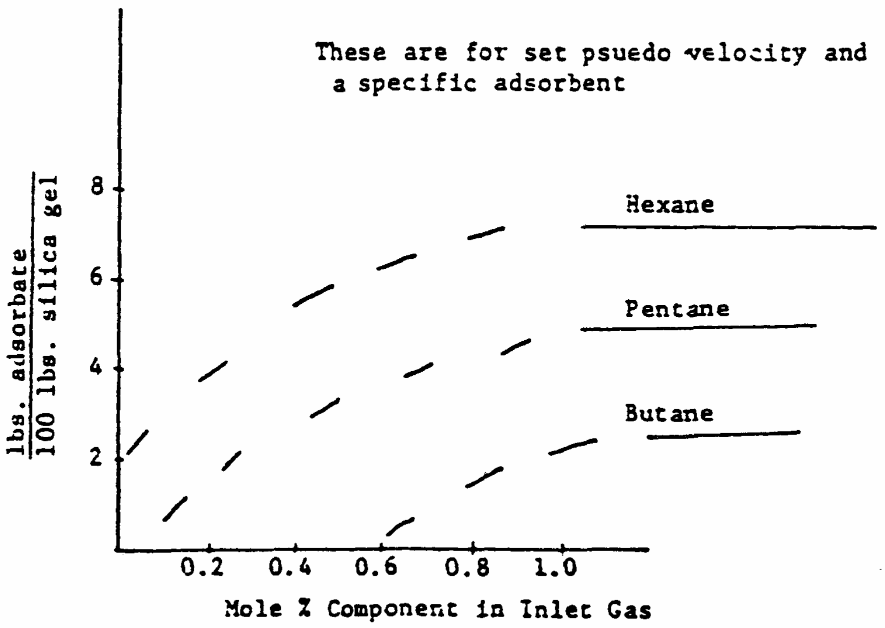


Figure 7.41: Component Adsorption Data

For propane and butane the amount of adsorption can be calculated from the following equations

$$\text{for } C_4,\ \log S = -\ 0.0988\ \frac{T}{M \log \frac{k}{y}} + 0.7770$$

$$\text{for } C_3,\ \log S = 0.0765\ \frac{T}{M \log \frac{k}{y}} + 0.6098$$

where:

S = component saturation US gallon/100 lbs adsorbent

T = absolute temp. °R

M = molecular weight of Component

k = Vapour Liquid Equilibrium constant

y = Mole fraction of component in the inlet gas

If we wish to find the length, set percent recovery, find amount of to be adsorbed in cycle time, usually 20 to 30 minutes, then from equilibrium curves or equations the quantity of adsorbent is determined by adding the quantity required for each component. The velocity of the gas sets the diameter. It is usually about 40-45 ft/mm. as a superficial velocity. Thus the length can be determined.

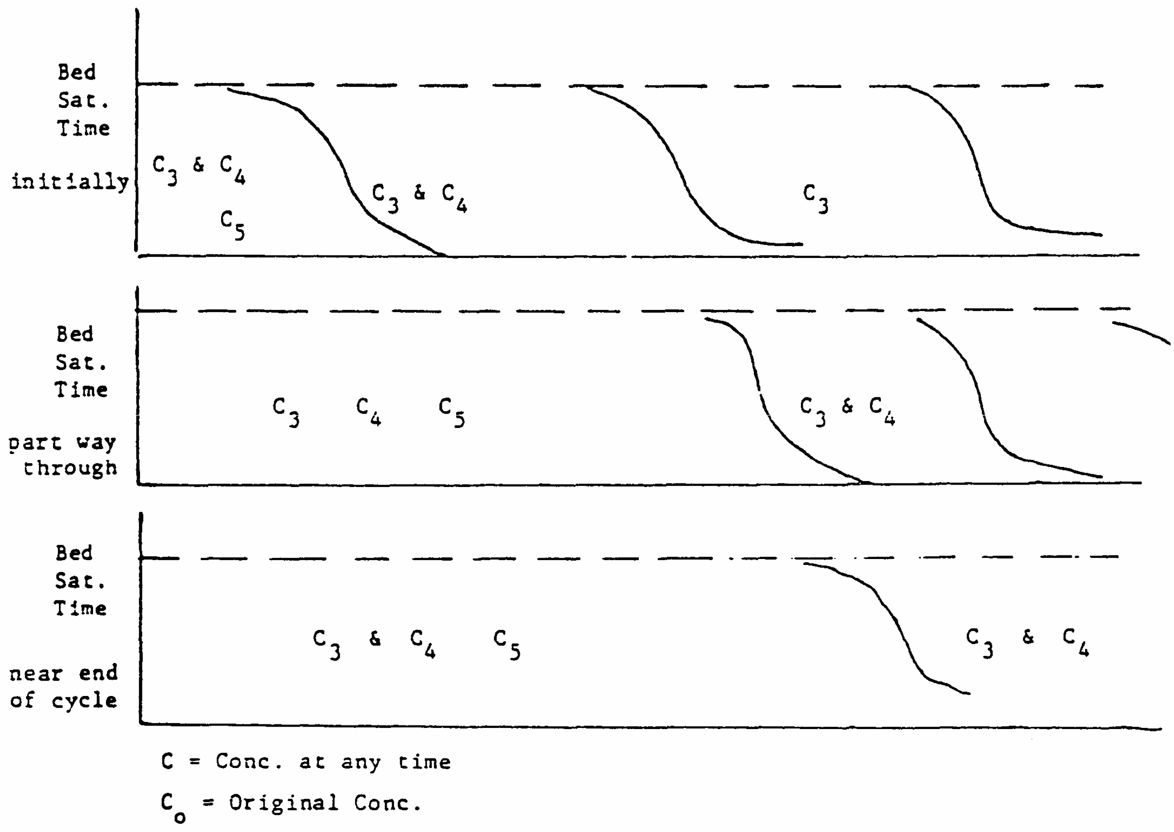


Figure 7.42: Adsorption Progress with Time

7.12 Example Problems

Example Problem 7.3

A debutanizer is designed so that the overhead product has only 2% of isopentane in it and the bottom has only 3% n-butane in it. The design feed composition and the top and bottom composition is given in the table below. During the operation of the tower the feed composition is changed to that also shown in the table. Determine what the increase in ref lux ratio has to be to make the separation.

Comp.	Moles Design Feed	New Feed Moles	Overhead Moles 100	Bottom Moles 100 Design	Bottom Moles 100 New Feed
C_3	0.5	0.5	0.5	----	----
iC_4	10.5	10.5	10.5	----	----
nC_4	20.0	20.0	17.9	2.1	2.1
iC_5	8.5	21.0	0.6	7.9	19.9
nC_5	10.5	20.0	----	10.5	20.5
C_6	10.5	12.0	----	10.5	12.0
C_{7+}	18.5	6.5	----	18.5	6.5
C_8	21.0	9.5	----	21.0	9.5

The tower has 17 actual trays. Assume that the tray efficiency is 70%. The tower operating pressure is 100 psia. The average temperature is 150°F which is the feed temperature. Tower top temperature is 120°F.

Example Problem 7.4

A fractionation tower is designed to split a feed (as given in the Table) into a top and bottom product, the composition of which are also given in the Table.

Mole Percent

Comp.	Feed	Top Product	Bottom Product
iC_4	10.0	15.3	----
nC_4	15.0	22.7	----
iC_5	17.0	25.8	----
nC_5	23.0	33.2	2.9
C_6	25.0	3.0	67.6
C_7	10.0	----	29.5
Total	**100.0**	**100.0**	**100.0**

The minimum reflux based on the overhead products is 4 to 1. An existing condenser is to be used that has a duty such that it is able to totally condense 7 times the amount of overhead product produced. This condenser will condense the overhead product 100°F using cooling water.

Calculate the number of actual trays required for this separation. Assume an overall tray efficiency of 75%.

Example Problem 7.5

It is planned to install a depropanizer the split as given in the table below.

Comp.	Feed Moles	Overhead Moles / 100 mole feed	Bottom Product Moles / 100 mole feed
C_2	4.0	4.0	----
C_3	40.5	39.0	1.5
iC_4	10.5	1.0	9.5
nC_4	16.4	----	16.4
iC_5	10.7	----	10.7
nC_5	8.9	----	8.9
C_6	9.0	----	9.0

The minimum reflux ratio for the separation is 1.8. Determine how many trays are required in the tower.

Data

A tower with an actual reflux ratio 1.3 times the minimum costs $500,000. Each tray more than required with the 1.3 times the minimum actual reflux cost $30,000 extra to install, including all auxiliaries.

The overhead product to be produced is 25,000 BPD. Extra trays are to be added if they pay out in the fuel savings obtained by reducing reflux requirements. The pay out time is to be 2 years to less.

The heat of condensation of a barrel of overhead product is 33,000 BTU's/BBL.

The cost of fuel is $1.00/MMBTU's delivered to the plant. Assume the fuel is burned in a furnace that is 75% efficient.

The tower is operating at a pressure of 200 psia. The tower average temperature is 160°F.

Assume the tower operates 350 days/year. Assume the trays are 80% efficient.

Example Problem 7.6

An existing absorption unit handles 300 MMSCFD at 14.4 psia and 60°F of gas of the analysis given below. It is operated at an average temperature of 80°F with 160 MW oil. It is proposed to increase the recovery of propane and heavier by using a lower molecular weight oil of 100 MW chilling the oil and gas so that the average tower temperature is 0°F. The oil circulation rate is to remain the same (i.e. the same (GPM). The cost of this revamp is estimated to be $6,000,000. If propane is worth $7.00/Barrel, C_4's are worth $7.70/BBl and C_5^+'s are $9.50/BBl, determine the payout for the proposed facility.

Gas Analysis

Comp.	Moles
C_1	91.34
C_2	5.27
C_3	1.92
iC_4	0.32
nC_4	0.60
iC_5	0.15
nC_5	0.18
C_6	0.22

Assumptions

a) The value of the C_3 and heavier in the gas is $1.05/MM BTU's.

b) The extra operating costs, except raw materials costs, are considered negligible.

c) The present unit is designed for 40% C_3 recovery. The oil rate is minimum for this recovery.

d) The tower operating pressure is 600 psia.

e) Assume P_K for any calculation of 2000 psia.

f) Assume just pure products recovered, i.e. do not calculate impurities of commercial C_3, C_4, etc.

Example Problem 7.7

A rich oil of the following composition is fed to a stripping tower with 8 theoretical trays.

Comp.	Mole %	Moles/Day
C_3	12.0	----
iC_4	4.2	----
nC_4	5.6	----
iC_5	2.7	----
nC_5	3.0	----
C_6	2.3	----
Lean Oil	70.2	----
	100.0	**10,000**

You are to find the amount of 18 mole wt. stripping gas (in SCFD) to remove most of the butane and lighter, i.e. 90% of the nC_4. The average tower pressure is 200 psia. Temperature at the top is 220°F and temperature at the bottom is 400°F.

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8.0 Heat Transfer

- General theory and types of heat transfer.
- Types of equipment and equipment design criteria.

8.1 Introduction

This is the transfer of energy between a source and a sink. We are primarily interested in the rate of transfer so that we can size equipment for heat transfer properly. There are three types of heat transfer[4].

8.1.1 Conduction

The transfer of heat from one part of a body to another part of the same body or from one body to another in physical contact with it, without appreciable displacement of the particles of that body. For steady state conduction the rate equation of

Equation 8-1

$$Rate = \frac{\text{driving force}}{\text{resistance}}$$

or

$$dQ = KA\frac{dt}{dx}$$

where:

dQ = heat transfer rate.

K = thermal conductivity.

A = area of transfer.

dt = temperature difference.

dx = thickness of place in which the transfer is taking place.

or integrated at a steady state

Equation 8-2

$$Q = \frac{K}{x}A(t_1 - t_2)$$

Figure 8.1 shows the system.

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[4] The student should read and study in some detail: Chapter 8 - Fired Equipment, Chapter 9 - Heat Exchangers and Chapter 10 - Air Cooled Exchangers of the new English GPSA Data Book as a supplement to this chapter.

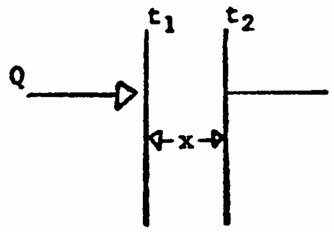


Figure 8.1: Heat Transfer System

The value of K depends on material:

For insulators - very low.

For conductors - very high.

8.1.2 Convection

This is the transfer of heat from one point in a fluid to point in the fluid. Natural convection occurs when there is no except because of heat transfer. Forced convection occurs when in motion, i.e. pumped or agitated. This type of transfer is expressed by the equation

Equation 8-3

$$dQ = hAdt$$

where:

A = area of transfer.

dt = the temperature difference.

h = a film coefficient which depends on fluid flow rate, the fluid properties, etc.

This is the type of heat transfer is mostly encountered in gas processing.

8.1.3 Radiation

This is the transfer of heat from one body to another not in contact with it by means of wave motion. This heat transfer is expressed by the Boltzmann equation:

Equation 8-4

$$dQ = \sigma\varepsilon\, dA\, T^4$$

where:

σ = a constant

ε = emissivity for the substance involved

T = the absolute temperature.

dA = the differential area from which heat transfer takes place.

the "ε" needs defining. It is the actual amount of energy that is absorbed or radiated as compared to a black body which has the value unity.

The transfer of heat between two surfaces can be expressed as:

Equation 8-5

$$Q_{12} = 0.173\,A_1\left[\varepsilon_1\left(\frac{T_1}{100}\right)^4 - \alpha_{12}\left(\frac{T_2}{100}\right)^4\right]$$

or in metric

$$Q_{12} = 2.06\,x\,10^7\,A_1\left[\varepsilon_1 T_1^{\,4} - \alpha_{12} T_2^{\,4}\right]$$

α_{12} = absorptivity at point 2

Quite often $\alpha 12 = \varepsilon 1$ and the equation can be simplified.

Figure 8.2 shows the system for which the equation applies.

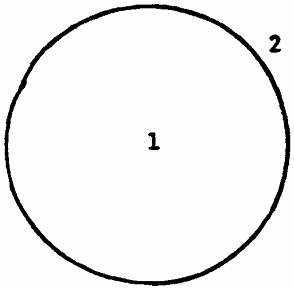


Figure 8.2: Radiation System

Both convection type heat transfer and radiation type heat transfer will be considered later in this section.

8.2 Heat Exchange Equipment

There are many types of heat exchange equipment. A few of the more important types are given in the following discussion.

Double Pipe Exchanger

One pipe inside the other, used in small size, 300 ft^2 (28 m^2) or lower.

Shell and Tube Exchanger

Many tubes inside a single shell. Figure 8.3 shows the many types of flow that can be expected in shell and tube exchangers. Also Figure. 8.6 in the GPSA Manual shows some other configurations. These can be divided mechanically as follows:

1. Fixed Tube Sheet - cannot remove tube bundle and thus cannot clean mechanical outside surface of tubes. Use in clean services:
    - LPG service
    - Sweet gas to gas exchangers
2. Floating Head Exchangers - can remove tube bundle and clean outside of tube surface. Use in dirty services:

- Sour condensate
- Rich/lean Amine

3. U Tubes - can remove tube sheet and clean shell side satisfactorily but need clean tube fluid. Used mainly in reboiler service:
    - Amine still reboiler

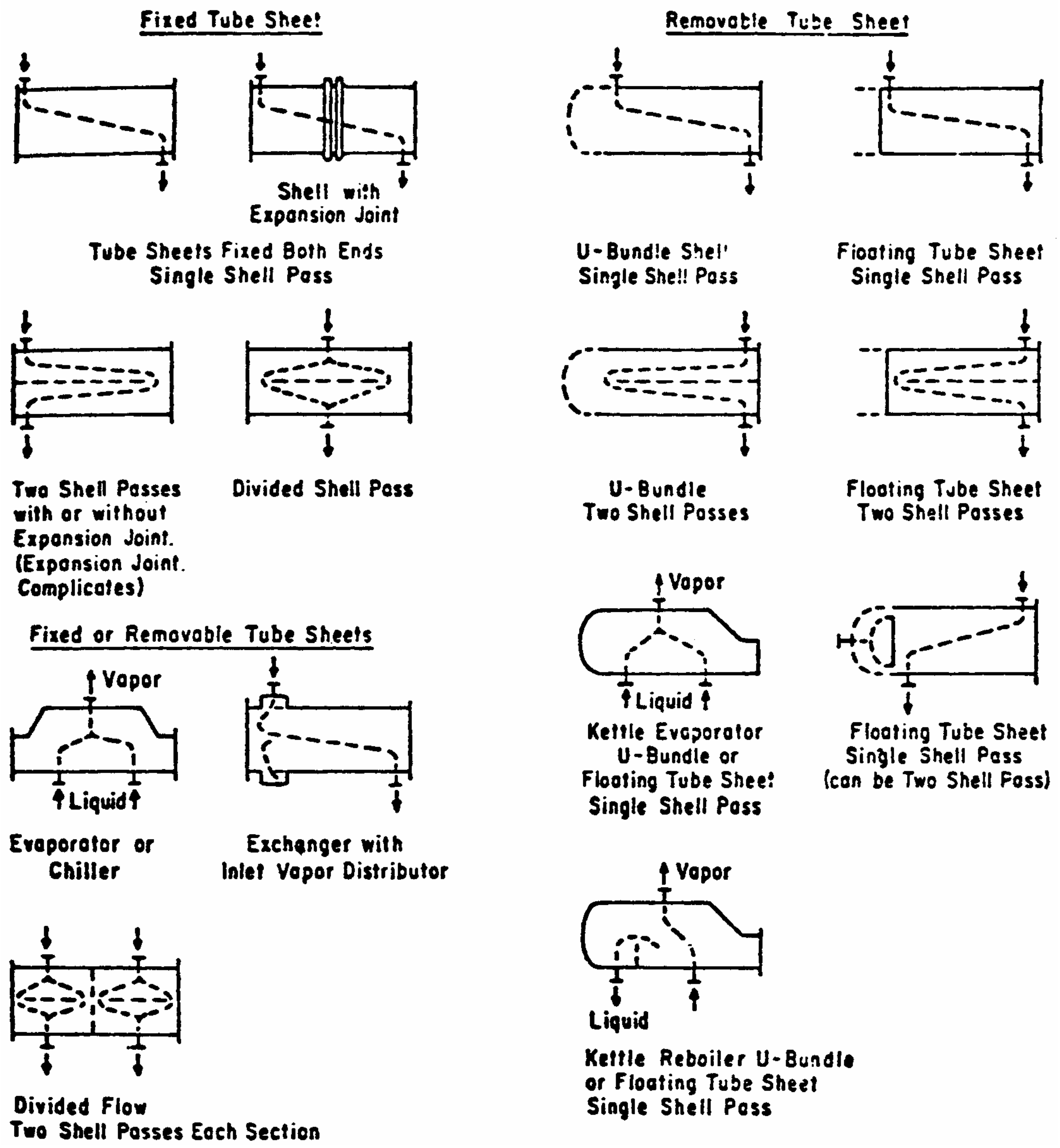


Figure 8.3: Shell and Tube Heat Transfer Equipment

8.2.1 Other Liquid to Liquid Exchangers

Other liquid to liquid exchangers sometimes used are:

1. Coil in box exchangers

2. Trombone exchangers (Falling film on outside of pipes).
3. Plate and fin - a series of corrugated fins and a plate as shown in Figure 8.4.

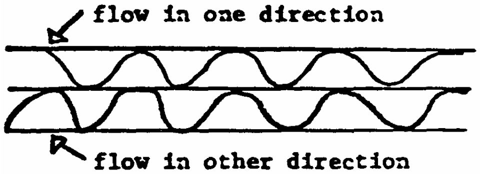


Figure 8.4: Plate and Fin Liquid to Liquid Exchanger

8.2.2 Air Exchangers

In this case air is used instead of water as the cooling medium. These units consist of a finned tube section in which the fluid to be cooled is sent through and a fan which either blows air through the tubes or induces it through same.

There have been many problems in locating these units properly in plants because of recirculation problems. Often stacks have to be put on these exchangers to make sure recirculation is minimized. The choice between Air Cooling and Water Cooling requires close study.

Water Cooling gives lower temperatures and thus lower operating pressure but generally requires a cooling tower.

When Air Cooling is used higher operating pressures are needed. This is particularly costly when refrigeration compressors are needed. Figure 8.5 shows some details of aerial coolers.

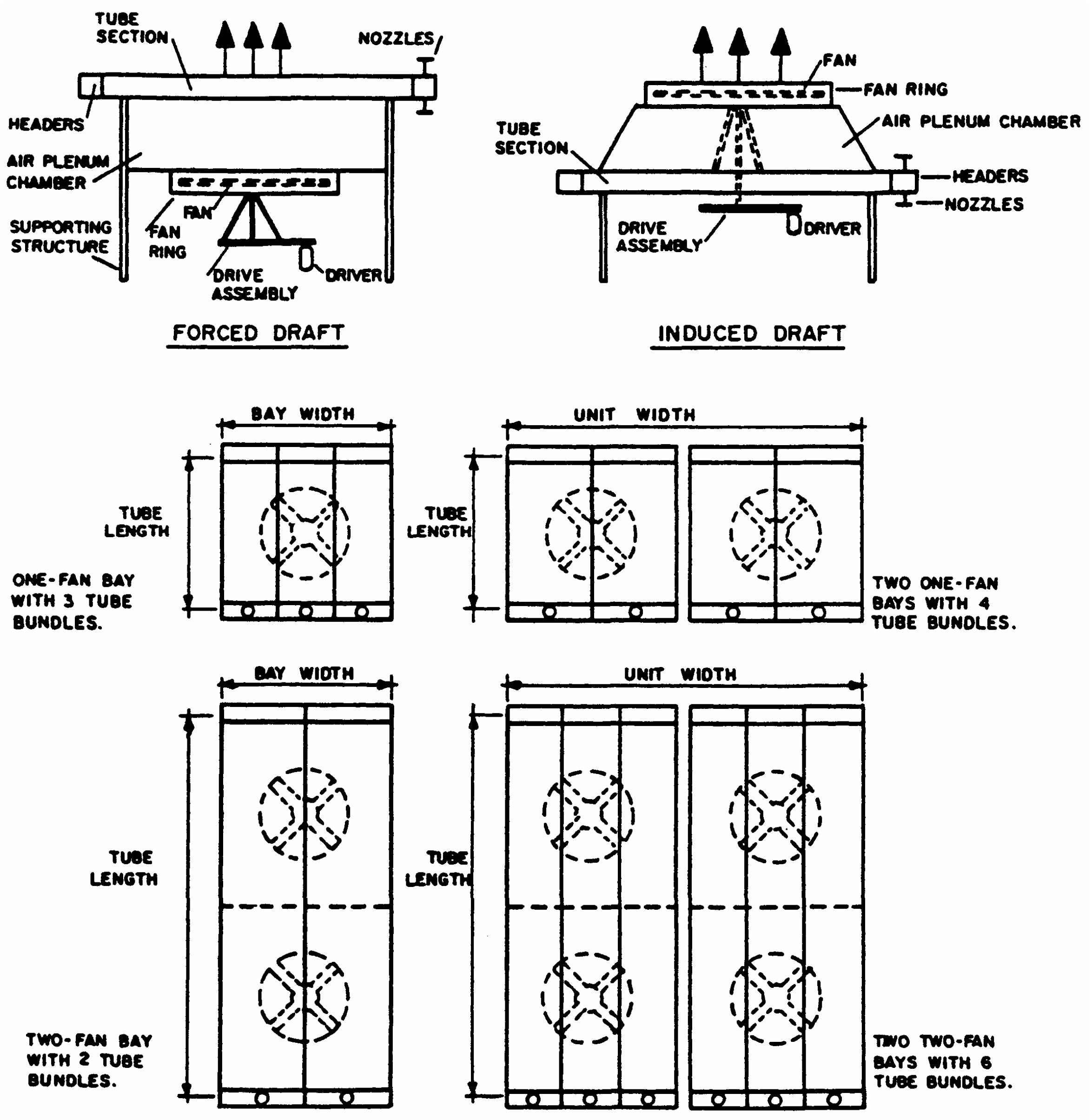


Figure 8.5: Aerial Coolers

8.2.3 Costs

The relative costs of the various exchangers considered are given in the table below.

Table 8.1: Exchanger Costs

Exchanger Type	Relative Cost in Carbon Steel
Fixed tube sheet	1.0
Floating Head Tube Sheet	1.28
U Tube	1.08
Kettle type U Tube with enlarged shell	1.2 - 1.4

Double Pipe	0.8 - 1.4
Pipe Coil	0.5 - 0.7
Open Tube Section Water Cooled	0.8 - 1.1
Open Tube Section Air Cooled	0.8 - 1.8

8.2.4 Furnaces

There are of course, many types of furnaces. Generally they look like:

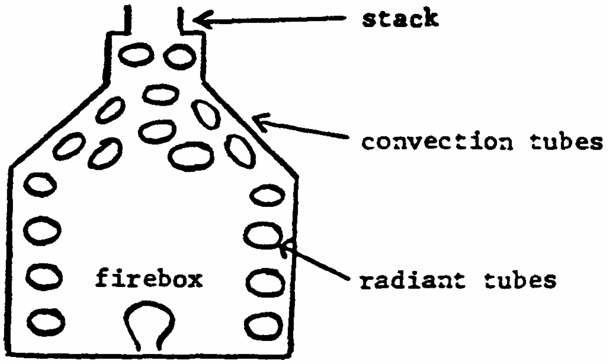


Figure 8.6: Typical Furnace

A good conservative design is to use 10-12,000 BTU/square feet (110,000-130,000 kjoules/m^2) as a heat flux in the radiant section.

Furnace design is a special science which has many problems, such as:

- Whether to put tubes vertical or horizontal.
- How far away from tubes should the fire be.
- The tube material - close review should be made to see if really carbon steel should be used. Often some type of alloy is worthwhile because of its longer service life.

8.3 Equipment Sizing

8.3.1 Heat Exchangers

In most cases in gas processing the equipment used for heat transfer uses convection as the primary method of heat transfer. Generally the following equation expresses the mechanics:

Equation 8-6

$$Q = UA\Delta T$$

where:

Q = heat transfer rate BTU/hr (Watts)

A = area required for transfer ft^2 (m^2)

U = overall heat transfer coefficient in $\dfrac{Btu's}{hrft^2\ °F}\ \dfrac{Watts}{m^3\ °C}$

ΔT = the temperature difference °F (°C)

The size of the equipment required is determined by the area "A" for heat transfer. This is generally what is to be determined. Let us then consider the other items in the equation.

Q - This is determined by a heat balance around the exchanger, i.e. by the equation:

Equation 8-7

$$Q = WC_P\left(T_1 - T_2\right) = W\left(H_1 - H_2\right)$$

where:

W = mass flow rate.

C_P = the specific heat.

T_1 = the entrance temperature on one side of the exchanger.

T_2 = the exit temperature from the same side of the exchanger.

H_1 = Enthalpy of material at temperature (T_1) (and pressure P_1 if a gas).

H_2 = Enthalpy of material at temperature (T_2) (and pressure P_2 if a gas).

ΔT - First let us review the temperature in a double pipe exchanger as shown in Figure 8.6. In this case we have what is called true counter flow.

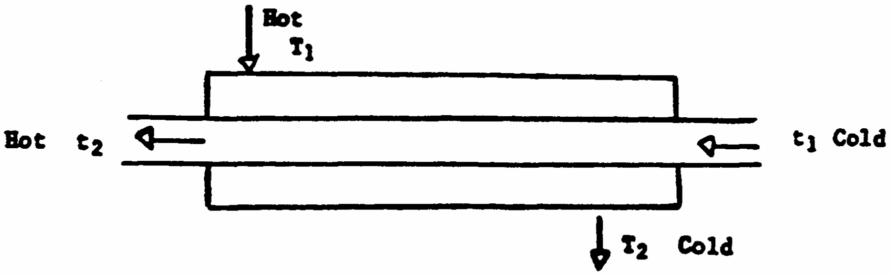


Figure 8.7: Counter Current Exchanger

To determine the average temperature difference for the exchanger shown in Figure 8.6 we use the equation given below:

Equation 8-8

$$\Delta T_{LMT} = \frac{\left(T_1 - t_2\right) - \left(T_2 - t_1\right)}{\ln \dfrac{T_1 - t_2}{T_2 - t_1}}$$

or

Equation 8-9

$$\Delta T_{LMT} = \frac{\Delta T_{HOT\ END} - \Delta T_{COLD\ END}}{\ln \dfrac{\Delta T_{HOT\ END}}{\Delta T_{COLD\ END}}}$$

This equation can be proved to apply for both counter current and parallel flow. Figure 8.1 on page 8.2 of the GPSA Data Book solves this equation for us graphically.

We have another problem in regular shell and tube heat exchangers. That is, we do not have true counter or co-current flow.

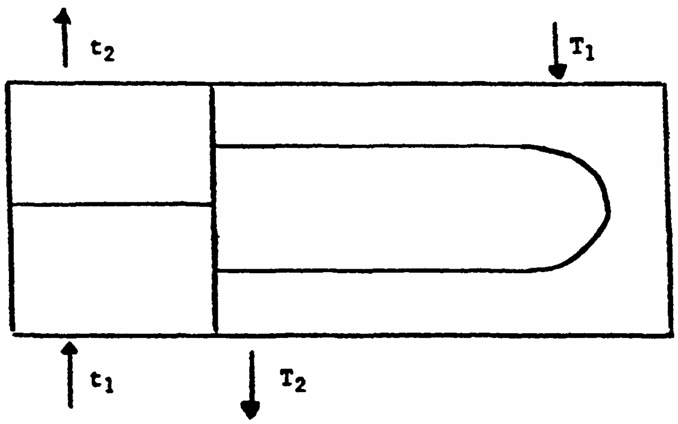


Figure 8.8: Typical Exchanger Configuration

For example we have some cross flow, some counter flow, some cocurrent flow. For this a factor by which the true log mean temperature is multiplied, is calculated. This factor is a function of the terminal temperature and the number of shell passes and tube passes. The average temperature is given by:

Equation 8-10

$$\Delta T_M = F \Delta T_{LMT}$$

where:

F = a factor which is determined from the ratio of temperature difference on each side of the exchanger "R" where

$$R = \frac{T_1 - T_2}{t_2 - t_1}$$

and temperature efficiency P which is the tube side temperature difference divided by the difference between the hot temperature entering the exchanger and the cold temperature entering the exchanger. ie.

$$P = \frac{t_2 - t_1}{T_1 - t_1}$$

ΔT_{LMT} is the true log mean temperature.

The charts on pages 8-3 and 8-4 of the GPSA Data Book cover the important cases for determining F. The charts on pages 9-5 and 9-6 of that manual should be used for air exchangers.

The most important item in an exchanger sizing is "U". This is normally determined by the exchanger manufacturer for the conditions given in a specification sheet. However, a knowledge of overall U's is of particualr value to the gas engineer. Figure 8-6 and Figure. 9-5 of the GPSA Data Book gives some common values to be expected. These are somewhat conservative. To see how the U is determined we will review how U is calculated. In a heat exchanger the heat transfer rate across a tube can be given by:

Equation 8-11

$$\frac{1}{U_0} = \frac{1}{h_0} + \frac{1}{h_i}\frac{D_0}{D_i} + R$$

where:

U_O = overall heat transfer area based on outside of tube surface.

h_O = film heat transfer coefficient based on the outside of tube surface.

R = fouling factor as given in the TEMA ratings and discussed later.

For determining h_O and h_i there are several empirical equations. The GPSA Data Book gives a chart for determining h_i, Figure 9-7 on Page 9-8. Figure 8-8 gives the chart for h_O. We will review the method used and give an example problem. We are considering only heat transfer without a change of phase (i.e. no boiling or condensing).

h_i - the inside film coefficient. An equation that is often used is the Sieder and Tate equation[8]

Equation 8-12

$$\frac{h_i D_i}{K} = 0.027\left(\frac{D_i G}{\mu}\right)^{0.8}\left(\frac{C_P \mu}{K}\right)^{\frac{1}{3}}\left(\frac{\mu}{\mu_W}\right)^{0.14}$$

This equation has been expressed in graphical form by plotting

Equation 8-13

$$j \equiv \left(\frac{h_i D}{K}\right)\left(\frac{C_P \mu}{K}\right)^{-1/3}\left(\frac{\mu}{\mu_W}\right)^{-0.14}$$

versus the Reynolds Number. This is given as Figure 9-7 of the GPSA Data Book. The Parameter L/D is also shown on the chart.

where:

h_i = heat transfer coefficient BTU/hr/sq.ft/°F ($W/M^{2°}C$).

D = tube ID in feet.

K = fluid thermal conductivity BTU/hr/ft/°F.

μ = fluid viscosity $lbs/ft^2/hr$.

C_p = fluid specific heat BTU/lb/°F.

μ_w = viscosity of fluid at tube wall temperature $lbs/hr/ft^2$.

G = mass velocity $lbs/ft^2/hr$ (kg/m^2-s).

L = length of a single tube in ft.

Thus if we know the Re Number and the other fluid properties we can use Figure 9-7 in the GPSA Data Book and find h_i.

h_O - the outside film coefficient. To find h_O we use a similar type of equation of a slightly different form developed by Colburn[9].

The form is:

Equation 8-14

$$\frac{h_0 D_e}{K} = 0.36\left(\frac{D_e G_s}{\mu}\right)^{0.55}\left(\frac{C_P \mu}{K}\right)^{1/3}\left(\frac{\mu}{\mu_W}\right)^{0.14}$$

where:

D_e = equivalent diameter = $\dfrac{\text{4 x free area}}{\text{wetted perimeter}}$

G_s = $\dfrac{\text{Mass Flow}}{\text{shell cross flow area}}$

The shell cross flow area is found at the centre of the bundle and is given by the formula:

Equation 8-15

$$A_s = \frac{ID\left(C' B\right)}{P_T\left(144\right)}$$

where:

A_s = shell cross sectional area in ft^2.

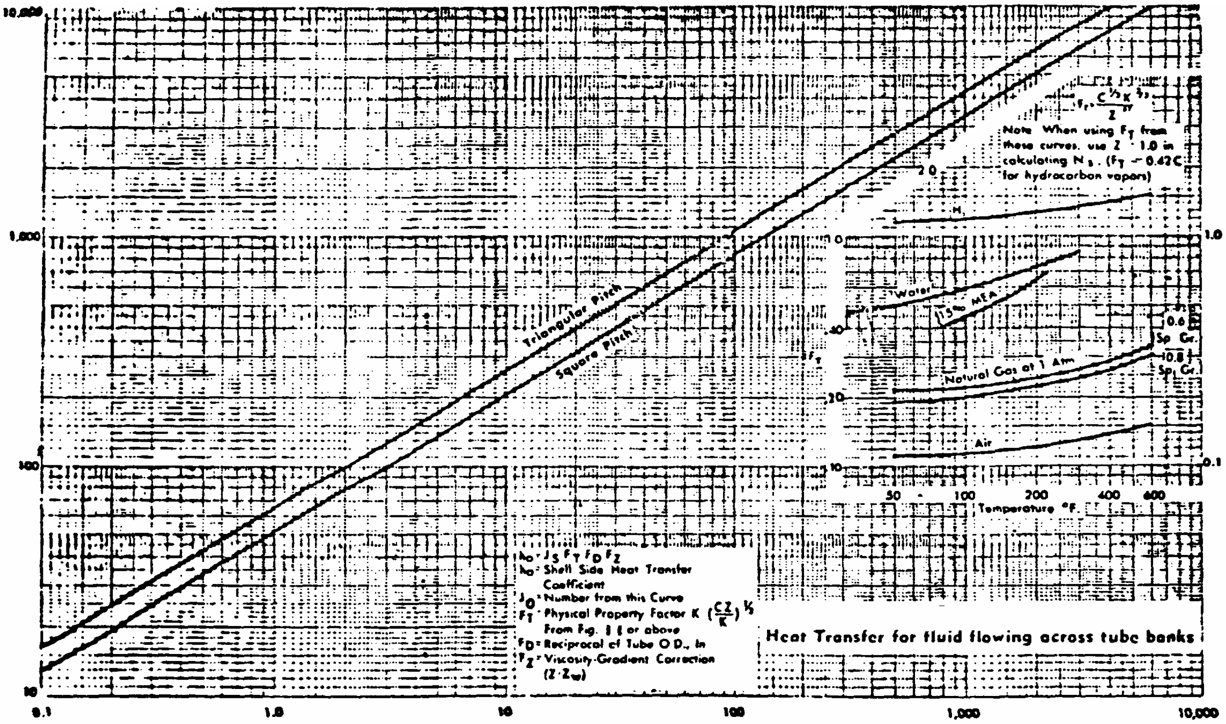
B = baffle spacing in inches.

C' = clearance between tubes in inches.

ID = shell ID in inches.

P_T = pitch (distance between centres of tubes).

$$J = \left(\frac{h_O d_O}{K}\right)\left(\frac{cz}{k}\right)^{-1/3}\left(\frac{z}{z_w}\right)^{-0.14}$$



$$N_S = \frac{D_O G_m}{z}$$

Figure 8.9: Heat Transfer for Fluid Flowing across Tube Banks

The figure below shows these symbols.

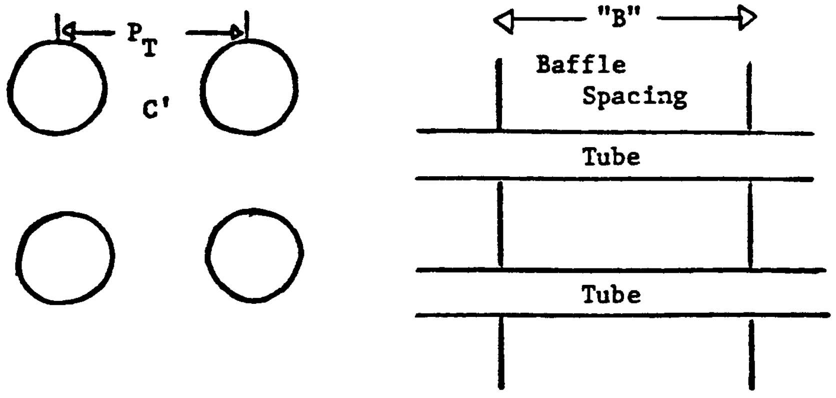


Figure 8.10: Tube Arrangement and Symbols

We then have a similar graph as for inside tubes (Figure 8.9, which is reproduced from an old edition of the GPSA Data Book. Z is used as a viscosity symbol) where j is plotted versus the Reynolds Number.

Equation 8-16

$$j = \frac{h_0 D_0}{K}\left(\frac{C_P \mu}{K}\right)^{-1/3}\left(\frac{\mu}{\mu_W}\right)^{-0.14}$$

Probably should use De but the figure has been corrected so as to use $D_{O'}$ which is the outside diameter of the tube.

For Shell and Tube exchangers the GPSA Data Book has developed a slightly different method of calculating the overall "U" (see pages 8-5, 8-6 and 8-7 of the GPSA Data Book). It is based on finding the resistance for both inside and outside tubes based on a set of standard values as given in Figure 8-8 on page 8-7 of the GPSA Data Book.

For example:

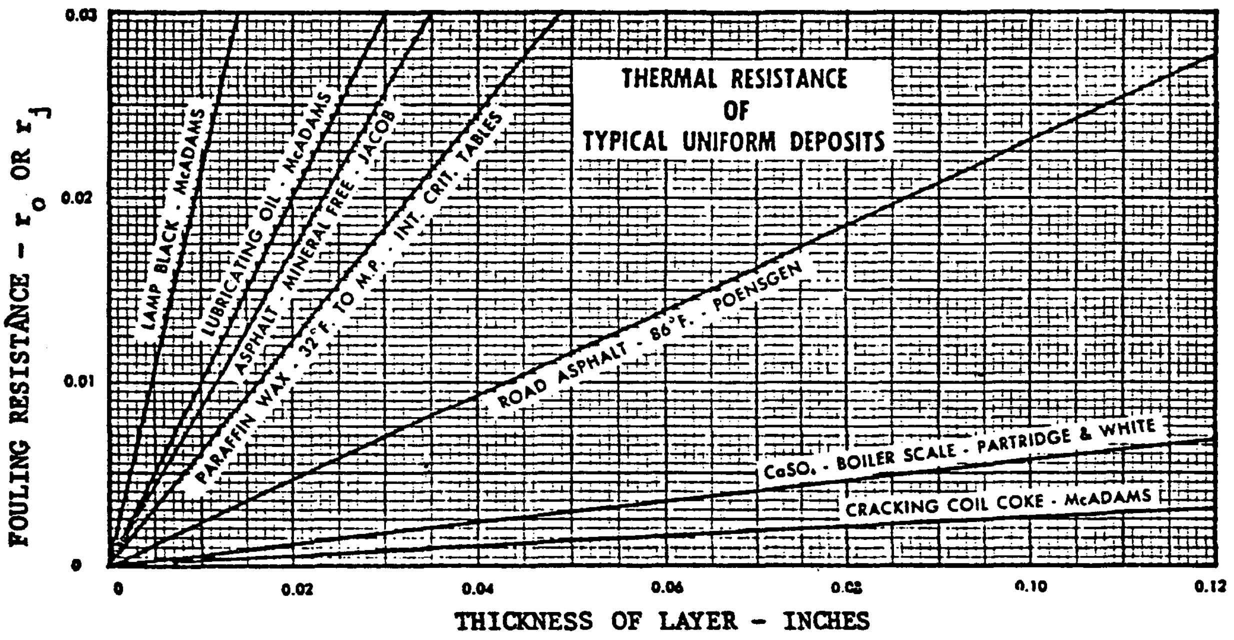


Figure 8.11: Thermal Resistance of Typical Uniform Deposits

$$r2_{TUBE\ SIDE\ NEW\ CONDITION} = f(r1)_{TUBE\ SIDE\ STANDARD\ CONDITION}$$

where:

f is for turbulent flow on the tube side.

Equation 8-17

$$f = \left(\frac{\mu_2}{\mu_1}\right)^{0.27} \left(\frac{K_1}{K_2}\right)^{0.67} \left(\frac{C_{P1}}{C_{P2}}\right)^{0.33} \left(\frac{G_1}{G_2}\right)^{0.8} \left(\frac{D_{02}}{D_{01}}\right)^{0.2}$$

A similar equation can be given for the shell side resistance. This is

$$f = \left(\frac{\mu_2}{\mu_1}\right)^{0.27} \left(\frac{K_1}{K_2}\right)^{0.67} \left(\frac{C_{P1}}{C_{P2}}\right)^{0.33} \left(\frac{G_1}{G_2}\right)^{0.6} \left(\frac{D_{02}}{D_{01}}\right)^{0.4}$$

where:

r_1 = the standard value at "1".

For pressure drop a similar set of ratios is given.

Please refer to Section 8 of the GPSA Data Book for further details; particularly Fig. 8-7 and Fig. 8-8 give tables of all standard relationships and values. When using this method the appropriate standard fluid, i.e. water, HC oil or methane, should be used.

8.3.2 Fouling Resistances

Effect of Fouling

Products of corrosion, dirt, or other foreign materials which deposit on heat transfer surfaces increase the overall thermal resistance and lower the overall heat transfer coefficient of the heat exchanger. Figure 8.10 which is from the TEMA Manual shows the effect of fouling thickness upon resistance for several types of deposits. In order that heat exchangers shall have sufficient surface to maintain satisfactory performance in normal operation, with reasonable service time between cleanings, it is important in design to provide a fouling allowance appropriate to the expected operating and maintenance conditions.

8.3.2.1 Considerations in Fouling Resistance Evaluation

The determination of appropriate values for fouling resistance involves both physical and economic factors, many of which vary from user to user, even for identical services.

Physical Considerations

Among physical factors influencing the extent of heat exchanger fouling are:

- Nature of fluid and material deposited
- Temperature of fluid
- Temperature of tube wall
- Tube wall, material and finish
- Fluid velocity
- Operating time since last cleaning

Economic Considerations

Economic factors entering into the determination of permissible extent of fouling are:

- Initial cost of exchanger
- Variation of cost with size
- Frequency of cleanings required
- Cost of cleaning, including loss of production
- Depreciation rate
- Tax rate
- Maintenance rate (exclusive of cleaning costs)
- Fluid pumping charges
- Desired net return on investment

8.3.2.2 Typical Fouling Resistances

The tables (given at the end of this chapter) present typical fouling resistances referred to the surface on which they occur. In the absence of specific data for setting proper resistances as described in the previous paragraphs, the user may be guided by the values tabulated on pages 43,44,45,46. In the case of inside surface fokling these values must be multiplied by the outside-inside surface ratio. Figure 10 shows how the fouling resistance builds up with layer thickness.

A more scientific approach to fouling resistance has been proposed in two articles by Taborek, Aohi, Ritter, Palen and Knudson[1]. They state that the basic fouling equation is as follows.

Equation 8-18

$$\frac{d(x_f K_f)}{dt} = \phi d - \phi r$$

where:

x_f = thickness of the fouling deposit.

K_f = the effective thermal conductivity of the fouling layer.

Φd = the rate of deposition.

Φr = the rate of removal.

or

Equation 8-19

$$\frac{dRf}{dt} = \frac{d(x_f K_f)}{dt}$$

where:

$\frac{d\ Rf}{dt}$ = net rate of fouling accumulation.

Many models solving this general equation have been developed.

These are given in the Table below. Taborek, Aohi, Ritter, Palen and Knudson discuss these models in some detail and present some experimental data on specific fouling test work. This reference should be contacted for more data on fouling.

Table 8.2: Comparison of Fouling Models

Model	Deposition Term Φ_d	Removal Term Φ_r	Characteristics of Fouling Type
Kern and Seaton	Proportional to concentration of foulant.	Proportional to fouling layer thickness and shear stress.	Sedimuntation. However, similar trends are seen with other types.
Watkinson	Proportional to concentration difference and to Arrhenius temperature values.	Used same as Kern and Seaton.	Reaction rate controlled or diffusion rate controlled (The two mechanisms were combined in an attempt to fit both decomposition and sedimentation data).
Reitzer	Proportional to supersaturation to the nth power.	None.	Combination of diffusion and reaction controlled.
Beal	Proportional to concentration gradient as function of tubulent and	None postulated. Assume all particles reaching wall stuck.	Deposition of dust from gas. However, neglecting removal makes model questionable for

	Brownian diffusivity.		high velocity and loose material.

8.3.3 Condensers

The same equation is used for sizing condensers as heat exchangers:

Equation 8-20

$$Q = UA\Delta T$$

and all the parts of the equation are determined as indicated in Section A. However, the film coefficient for condensing is determined from quite a different formula for determining "h_O". There are two types of condensing - dropwise of film.

Dropwise gives very high coefficient but requires special conditions. Usually film condensation is considered to take place. Generally the flow is laminar i.e. Reynolds No. is less than 2100. Also two types of situations exist as shown in Figure 8.12. In vertical tubes the flow is down the tube and accumulates as the condensate flows down the tube. In horizontal tubes it also accumulates when flow is inside and drops to the next tube when condensation is on the outside of the tubes.

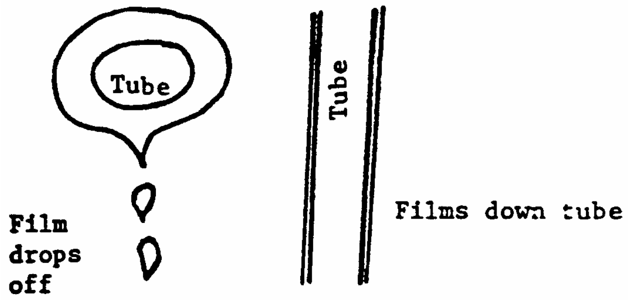


Figure 8.12: Condensing Methods

The equations that can be used for calculating "h" are as follows. For vertical tubes

Equation 8-21

$$h = 0.925\,K\left(\frac{g\rho_1^2}{\mu\Gamma}\right)^{1/3}$$

For horizontal tubes

Equation 8-22

$$h = 0.76\,K\left(\frac{g\rho_1^2}{\mu\Gamma}\right)^{1/3}$$

where:

h = heat transfer coefficient BTU's/hr/ft^2/°F.

K = thermal conductivity of liquid BTU/hr/ft°F.

g = gravity (4.18 x 10^6) ft/hr^2.

ρ_1 = density of liquid lbs/ft^3.

μ = viscosity lbs/hr/ft.

Γ = tube loading lbs/hr/ft.

These equations can be applied for both inside and outside tubes. The equation does assume that the flow of condensed fluid is laminar. The calculation of Γ is particularly important. In vertical tubes it can be calculated by just dividing the flow of condensed liquid by the tube perimeter. The equation to use is

Equation 8-23

$$\Gamma = \frac{W}{n\pi \frac{d}{12}}$$

where:

W = flow lbs/hr.

n = number of tubes.

d = diameter of tubes in inches.

When flow is in horizontal tubes, "Γ" may be found from

Equation 8-24

$$\Gamma = \frac{W}{2nL}$$

for inside tubes

where:

L = length of tube in feet.

For outside tubes

Equation 8-25

$$\Gamma = \frac{W}{4n_r L}$$

where:

n_r = no. of tubes at centre of exchanger.

Another important feature of condensers is to calculate the overall ΔT. This usually has to be found from a condensing curve when a multi-component mixture is being condensed. Figure 8.12 shows a typical condensing curve for an amine still overhead condenser.

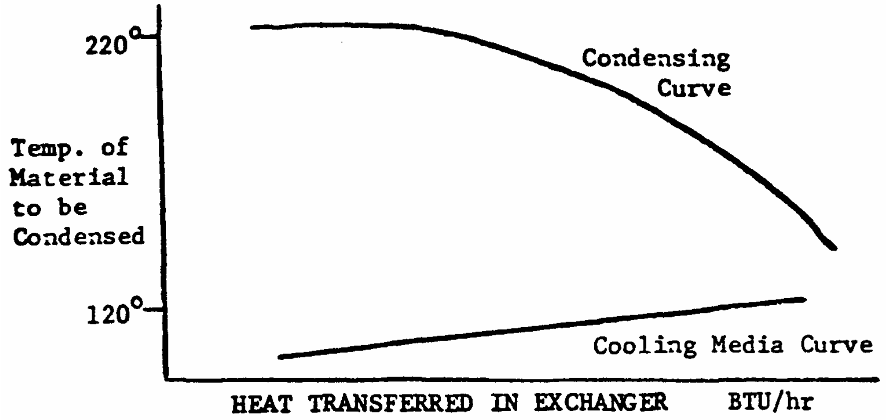


Figure 8.13: Multi-Component Condensing

The overall ΔT is found by breaking area into several sections and finding ΔT for each section and the area required for each section. The curve itself is calculated by determining amount of material that condenses at each temperature and the latent heat at that temperature.

Often in a hydrocarbon mix with only a few components the condenser entrance and exit temperatures can be found from the dew point and bubble point respectively and sometimes the log mean ΔT can be used as the average ΔT.

8.3.4 Reboilers

In this equipment we can again use Equation (7) if only convection heat transfer is experienced. However, the calculation of "h_O" is based on a different formula and, as will be seen shortly, often the heat flux Q/A is the limiting design criteria. For boiling liquids consider the conditions shown in Figure 8.13.

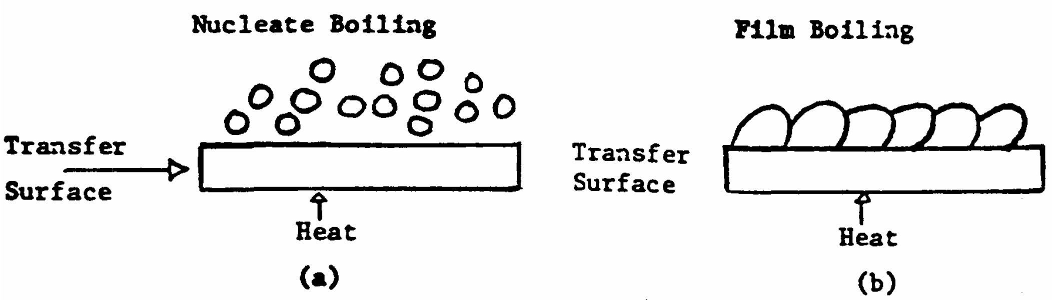


Figure 8.14: Types of Boiling

Very high values of h can be obtained in the boiling in the manner shown in Figure 8.14(a) but this is only for low ΔT. What happens is that film eventually blankets the boiling surface as shown in Figure 8.14(b). Thus $\frac{Q}{A}$ decrease for a while as $\Delta T_{solid\text{-}liquid}$ increases. This is shown in

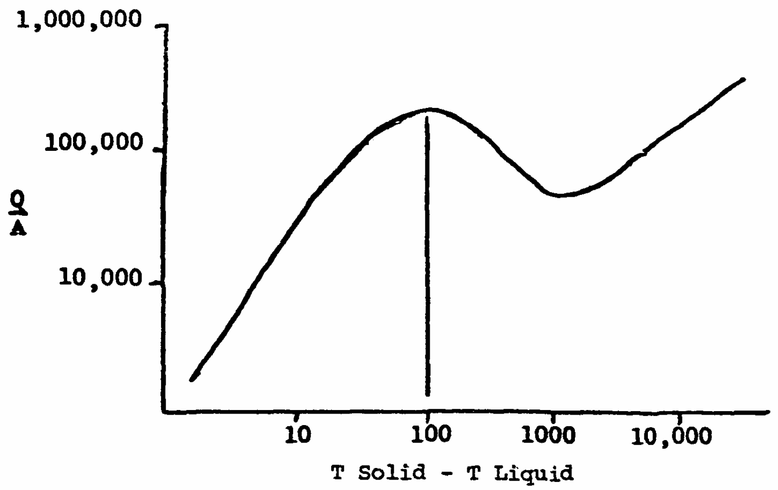


Figure 8.15: Heat Flux in Boiling

Thus we normally design reboilers for a heat flux. Kern[7] recommends the following values.

For natural circulation:

Q/A < 12,000 BTU/ hr/ ft^2 for organics (130,000 kJ/ hr/ m^2)

and

Q/A < 18,000 BTU/ hr/ ft^2 for water systems (194,000 kJ/ hr/ m^2)

For forced circulation, in which normally partial vapourization only occurs, higher fluxes can be used.

Q/A < 20,000 for organics (220,000 kJ/ hr/ m^2) and <30,000 for water systems (330,000 kJ/ hr/ m^2)

Please refer to the English GPSA ('87) for more specific heat flux ranges; particularly on Page 9-12.

Or the maximum flux can be calculated from the following equation:

Equation 8-26

$$\left(\frac{Q}{A}\right)_{\max} = 143\,\rho_V \lambda \left(\frac{\rho_L - \rho_V}{\rho_V}\right)^{0.6}$$

where:

λ = latent heat of evaporation.

ρ_V = density of vapour.

ρ_L = density of liquid.

The maximum temperature difference between the surface and the boiling fluid can be found from

Equation 8-27

$$(t_S - t_b)_{\max} = \frac{1}{m}\left(\frac{Q}{A}\right)_{\max}$$

where:

t_s = surface temperature °T.

t_b = boiling temperature.

m = a constant characteristic of the material being boiled. m is available from article by J.R. Fair.

This article also gives varying values of h_{br}, the boiling coefficient for various materials. It is a good article on reboilers in general.

Also, h for boiling can be calculated from the following equation:

Equation 8-28

$$\frac{h}{C_P G} = 4.02\left(\frac{DG}{\mu}\right)^{-0.3}\left(\frac{C_P \mu}{K}\right)^{-0.6}\left(\frac{P_L \chi}{p^2}\right)^{-0.425}\Sigma_L$$

The symbols are as given before and the units are as previously given and

where:

γ = surface tension dynes/cm.

P - = pressure psia.

Σ = surface condition factor 1.0 for steel or copper, lower for stainless steel.

Union Carbide has developed a new tube for boiling called a porous boiling tube (See Martin).

An excellent article on the types of heat exchangers just discussed is "Design of Heat Exchangers" by R.C. Lord, P.E. Minton and R.P. Slusser.

8.3.5 Air Exchanaers

In air exchangers the equation (6) is used.

ΔT is normally calculated for cross flow type of exchanger. The correction factor as obtained from Figures 9-3 and 9-4 in the GPSA Data Book on page 9-5 and 9-6 is used. *A* is usually expressed as a bare fin tube area. *U* is calculated as previously indicated for regular exchangers, i.e. Equation (11). The outside film coefficient for air can be found from Figure 9-9 on page 9-10 of the GPSA Data Book which plots h_O versus air velocity. An air velocity of about 675 ft. per minute is often used, which is equivalent to about 3000 lbs/hr ft^2 (4 kg/sec/m^2). Detailed comparison is made of pressure drop allowed on the air side versus the required area. For finned tubes the *h* can be found from the following equation:

Equation 8-29

$$\frac{h\,d_r}{K_a(12)} = 0.1378\left(\frac{d_r G_m}{12\mu}\right)^{0.718}\left(\frac{C_P \mu}{K_a}\right)^{1/3}\left(\frac{S}{l}\right)^{0.296} F_r$$

where:

h = coefficient of heat transfer for high fin tubes BTU/hr/sq ft/°F.

K_a = thermal conductivity of air BTU/hr/sq ft/°F/ft.

d_r = root diameter of tube in inches.

G_m = maximum flow of air at minimum area lbs/sec/ft^2.

C_p = specific heat of air (about 0.24 BTU/lb/°F).

S = distance between fins in inches S = 1-nt/n.

n = number of fins per inch.

t = fin thickness in inches.

ℓ = fin height in inches df - dr/2.

F_r = row factor from 0.810 for two rows to 0.987 for 20 rows.

See Example problem in GPSA Data Book starting page 9-7 on sizing aerial coolers.

8.3.6 Furnaces

Furnaces are normally sized by the heat flux allowable *Q/A* = . This is usually set between 10,000 to 15,000 BTU/hr/ft^2, generally 15,000 BTU/hr/ft^2 in the radiant section and 10,000 BTU/hr/ft^2 overall. This varies with the tube material used and fluid being heated. Most furnaces have both a convection section and radiant section. Figure 8.6 shows a typical furnace.

About 70% of duty is in the radiant section and about 30% of the duty is in the convection section. However, area in each section is about the same, the different sections use different equations for calculating the area.

Let us first consider the radiation section. The rate of heat transfer can be calculated from the formula:

Equation 8-30

$$Q_{Rr} = \sigma \alpha A_{cp} F \left(T_g^4 - T_t^4\right)$$

where:

Q_{Rr} = radiant heat transfer rate in radiation section.

σ = constant 0.173 x 10^{-8} BTU/hr/sq ft/°R.

A_{cp} = cold plane surface area sq ft. (total exposed tube surface area) (tube length times center to center distance).

α = a factor of comparison of what a tube sees in a furnace and given in Figure 8.16.

T_g = the gas temperature °R.

T_t = the tube temperature °R (add 100°F to average fluid temperature to determine this).

F = an exchange factor as given in Figures 8.16 and 8.17 and Figure 3 and Table 8.3.

To find this it is necessary to use "L" the beam length which is given in the next Table.

For convection in the radiant section the following equation can be used:

Equation 8-31

$$Q_{Rc} = h_{rc} A_{RT} \left(T_g - T_t\right)$$

Table 8.3: Beam Lengths for Gas Radiation

Dimension Ratio	Mean Beam Length, L
Rectangular Furnaces, Length-Width-Height, (In any Order)	
1-1-1 to 1-1-3	2/3 (Furnace Volume)$^{1/3}$
1-2-1 to 1-2-4	2/3 (Furnace Volume)$^{1/3}$
1-1-4 to 1-1-∞	1 x Smallest Dimension
1-2-5 to 1-2-∞	1.3 x Smallest Dimension
1-3-3 to 1-∞-∞	1.8 x Smallest Dimension
Cylindrical Furnaces, Diameter-Height	
1-1	2/3 x Diameter
1-2 to 1-∞	1 x Diameter

where:

Q_{RC} = convective heat transfer rate in radiation section.

A_{RT} = tube area in the radiant section.

h_{rc} = convective heat transfer coefficient usually about 2.0 BTU/hr/sq ft/°F

In the normal furnace A_{RT} is about 2 times αA_{cp} and F is often 0.57.

Q_{RC} can be expressed as

Equation 8-32

$$Q_{Rc} = 7.0\alpha A_{cp}\left(T_g - T_t\right)$$

For the convection section the regular method of finding the overall heat transfer coefficient can be used. To calculate the outside "h" the following equation is used.

Equation 8-33

$$h_{cc} = \frac{2.14\left(T_f\right)^{0.28}\left(G_{\max}\right)^{0.6}}{d^{0.4}}$$

where:

h_{cc} = convection section outside film coefficient.

T_f = average outside gas temperature.

G = mass velocity lb/sq ft/sec.

d = tube OD in inches.

A good article on rating fired heaters is one by R.N. Wimpress.

8.4 Specifying Exchangers

Let us now consider what normally people in the gas processing business wish to do. That is, specify an exchanger to fit a heat transfer application. Let us consider shell and tube exchanger only. Air coolers can also be specified in a similar manner. What must be specified:

- Process Conditions

- Physical properties of fluid involved
- Performance conditions
- Mechanical design conditions
- Materials of construction
- Codes

8.4.1 Physical Properties

If it is not a well known fluid, should tell exchanger manufacturer all about fluids, i.e. actual fluid, its gravity, viscosity, thermal conductivity, specific heat, etc.

8.4.2 Material of Construction

Specify for fluids involved (only if special materials required).

8.4.3 Codes

Normally unfired pressure vessel code of Province, and TEMA division, either R or C or B. All rather similar except B and C allow smaller diameter tubes.

8.4.4 Mechanical Design Conditions

Specify tube Φ and length, normally ¾” and either 16 or 20 ft. for U bundles or gas to gas exchangers which have 40 and 50 ft. Also tube layout and pitch (clearance between tubes) should be given. Figure 8.19 below explains this.

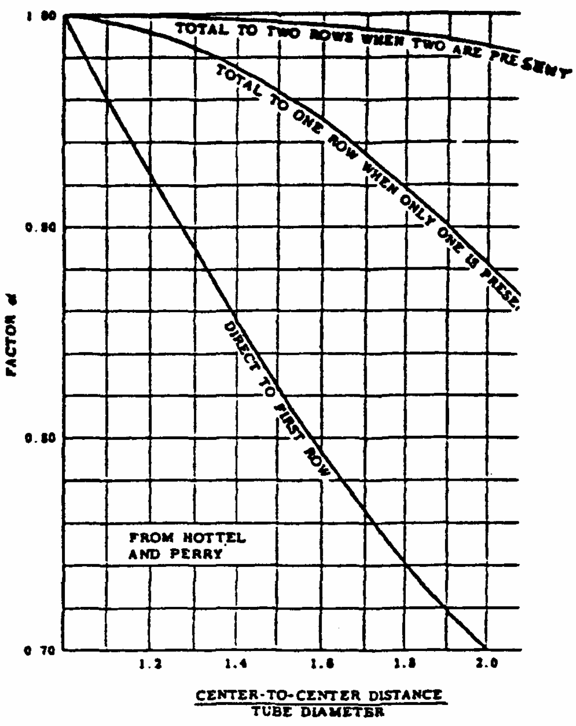


Figure 8.16: Absorption Efficiency of the Tube-banks

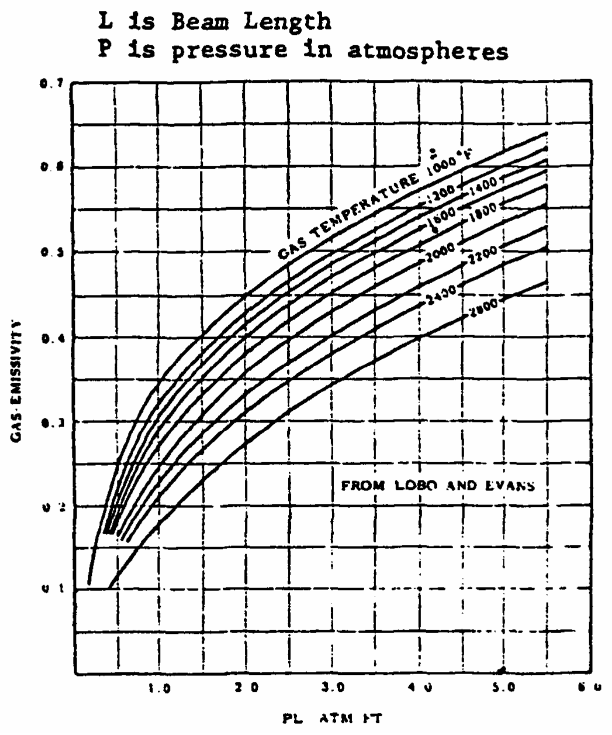


Figure 8.17: Gas Emissivity

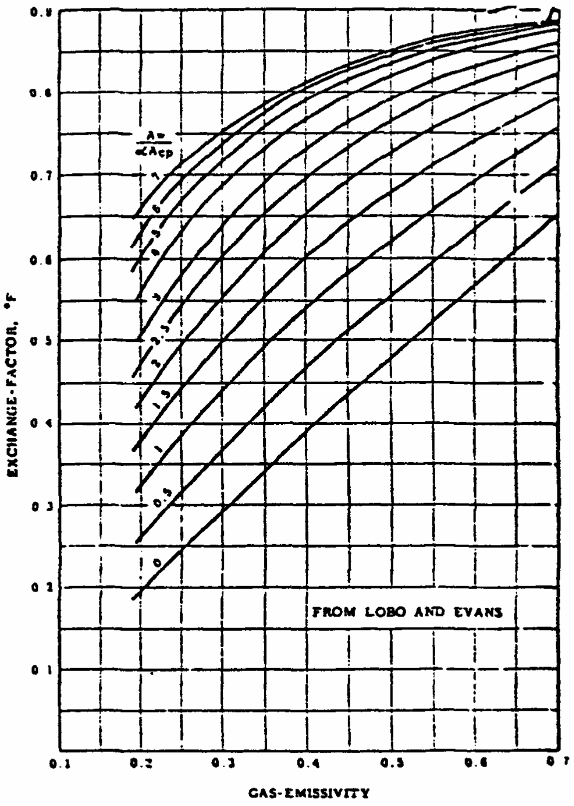


Figure 8.18: Overall Radiant Exchanger Factor

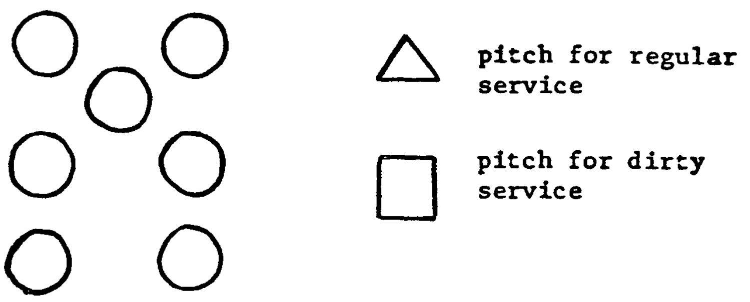


Figure 8.19: Tube Layouts

8.4.5 Performance Conditions

Overall heat transfer coefficient and the fouling factors. These are generally left up to exchanger supplier and checked by purchaser.

Listing in TEMA, given earlier, gives typical values for the fouling factor.

8.4.6 Process Conditions

This is the main part of the specifications for purchaser.

Heat Transferred

The quantity of fluid flowing is determined from plant process balance. Heat to be transferred from process balance, but modified for temperature limits, as discussed.

Pressure Drop

This is an economical consideration, pump capacity versus exchanger surface. (See GPSA Data Book for calculations of actual drop). Here are some guidelines:

		Normal Maximum Allowed
Exchanger	shell side	10 psi
	tube side	10 psi
Coolers	as above	
Condensers	shell condensing side	3 psi
	tubes, cooling side	10 psi
Reboilers	shell side, boiling	1 psi
	tubes side, condensing	1 psi
Chillers	same as reboilers	
Air Coolers	process side as above - air side, generally set velocity of air about 600 - 700 ft./min.	

Fluid Location

Some general rules are:

In Shell:

- Boiling liquid.
- Condensing liquid.
- Cleanest of two fluids.
- When no other considerations - hot fluid (handles expansion better).

In Tube:

- Dirty fluid.
- High pressure fluid.
- Condensing fluid when boiling a fluid.
- Corrosive fluid.
- When no other consideration — cold fluid.

Temperatures

These may be set by process balance but there are some special considerations:

Cooling with Water - Cooling water outlet temperature is set by scaling or corrosion conditions. This should be calculated by the stability index - see pages 11-9 and 11-10 in the GPSA Data Book. When this cannot be done do not go over 120°F (50°C). There is also an economic balance on how much to cool with water and how to cool with other fluids.

Economic Temperature Approach - It is necessary to consider what is the economic temperature of the other fluid in an exchanger. Let us consider separate types of heat exchanger equipment:

h) Condensers - a single component condensing; condenser temperature set by pressure of system, no sub-cooling considered. Figure 8.20 below shows this.

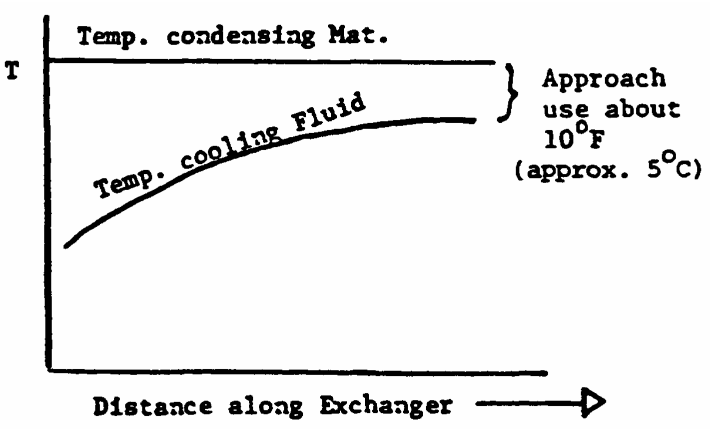


Figure 8.20: Single Component Condensing

a) Multi-Component - Condense to within 10°F (5°C) of cold fluid outlet temperature. No crossovers considered. Also we need a condensing curve in this case. Generally consider enthalpy of condensing i.e. for hydrocarbons use dewpoint at entrance to exchanger and bubblepoint at exit from exchanger.

b) Water Exchangers - Can heat up water to point that scaling starts unless water is treated. This is determined by stability index (Fig. 11-9 in GPSA Data Book). If no data, maximum temperature 120°F (50°C)

c) True Counter Current Exchangers - i.e. Gas to gas exchangers, double pipe exchangers. No problem with cross-overs here. If flow of fluids is quite different and there is a large difference in temperature at one end, approach can be brought to 10°F (5°C) at other end.

d) Cross Flow Exchangers - Consider the flow in the exchanger shown in Figure 8.21.

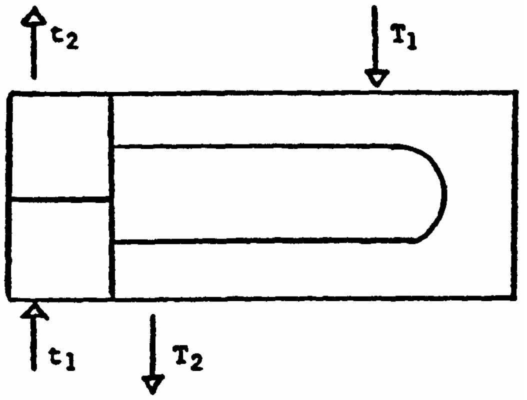


Figure 8.21: Crossflow Exchanger without Baffle

Without internal shell baffling T_2 could not be less than t_2 as there would be reverse of heat flow. If horizontal baffling is used we now have better counter flow as shown in Figure 8.22.

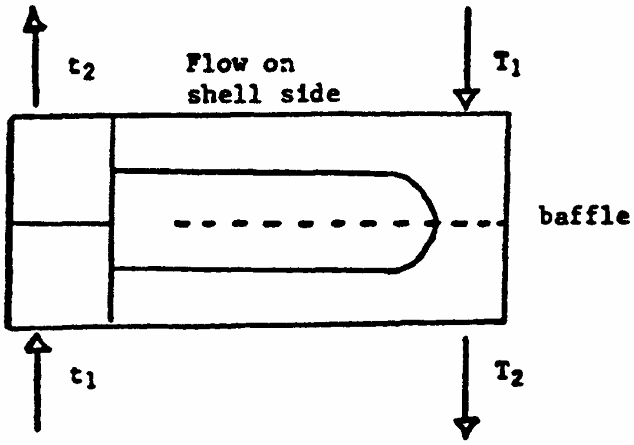


Figure 8.22: Crossflow Exchanger with Baffle

T_2 can be less than t_2. However you should be careful. Try to limit cross-over to less than 20°F (11°C) in a single shell.

e) Reboilers, Chillers - If one fluid is at constant temperature and the other is varied, i.e. chillers, steam heaters, etc., use 10°F (5°C) approach as shown in Figure 8.23.

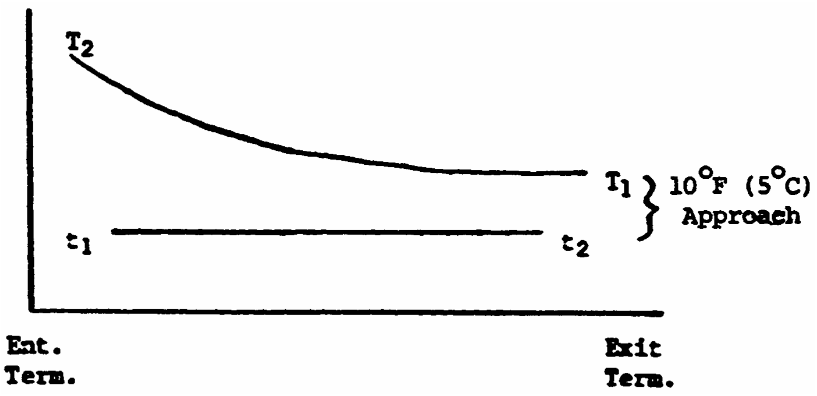


Figure 8.23: Chiller Temperature Curve

8.5 Heat Transfer to Buried Pipelines

The problem of designing systems such as heater or hot water tracing systems is actually calculating the loss of heat from the buried pipe and making sure the liquid flowing through it does not cool to a temperature below the hydrate formation temperature of the fluid. The length of line that can be used before reheating or how much the gas has to be heated can be calculated from the following equations (34) and (35).

Equation 8-34

$$Q = UA\frac{(T_1 - t) - (T_2 - t)}{\ln \frac{T_1 - t}{T_2 - t}}$$

where:

U = the overall heat transfer coefficient for transfer from buried pipes to the ground.

A = area of transfer, i.e. pipe perimeter times its length.

T_1 = the initial gas temperature.

T_2 = the final gas temperature. The final temperature is some temperature above hydrate point (usually about 5°F).

Q = the rate of heat transfer at steady flow rates BTU's/hr.

t = the ground temperature.

and

$$Q = WC_P(T_1 - T_2)$$

or using enthalpies as Cp are not readily available = W (H_1 — H_2)

Equation 8-35

$$Q = W(H_1 - H_2)$$

where:

W = the rate of flow, lbs/hr.

Cp = the specific heat of gas.

T_1 = as previously — initial gas temperature.

T_2 = as previously — final gas temperature.

H_1 = enthalpy of material at initial gas temperature.

H_2 = enthalpy of material at final gas temperature.

The overall heat transfer coefficient, U's value, varies considerably with the soil conditions. The table below gives some experimentally determined values.

Table 8.4: Overall Heat Transfer to Ground

Soil	BTU/hr/ft^2/°F	(W/m^2/°C)
Clay and gravel	0.618	(3.51)
Shale and muskeg mix	0.500	(2.84)
Muskeg	0.400 (after system stabilized and muskeg around pipe dried)	(2.27)
	2.000 (Wet)	(11.30)
Silty gravel	0.600	(3.41)
Wet soil	1.500	(8.52)

A good design value is 0.65 BTU/hr/ft^2/°F (3.69 W/m^2/°C).

If insulated pipe is used a design value of 0.15 BTU/hr/ft^2/°F

(0.85 W/m/ft) for overall heat transfer coefficient can be used. Field tests show that the actual values generally run a little lower than this (down to 0.10).

Example Problem 8.1

Calculate the area required for a rich to lean amine exchanger that is to heat the rich amine from 140°F to 210°F using lean amine at 255°F. The rich amine flow is 1700 US gpm and the lean amine flow is 1600 US gpm. For simplification assume the properties of rich and lean amine are the same, i.e. the specific gravity of the amine solution is 1.020 and the specific heat at average conditions for both products is 0.95.

1. Find outlet temperature of lean amine.

$$1700(8.33)(1.020)(60)(.95)(210-140)$$

$$= 1600(8.33)(1.020)(60)(.95)(255-t)$$

$$t = 181°F$$

2. Find the log mean temperature

$$\Delta T = \frac{(255-210)-(181-140)}{\ln\frac{45}{41}} = 43$$

7. Find the heat duty (amount of heat to be transferred).

$$Q = 1700\,(8.33)(1.020)(60)(0.95)(210-140) = 57{,}000{,}000 \text{ BTU}$$

8. Find the area required

$Q = UA\Delta T$

$A = Q/U\Delta T$

Now U from NGPSA book Figure 8-6 on page 8-5 = 130.

$$A = \frac{57{,}000{,}000}{130(43)}$$
$$= 10{,}200\ ft^2$$

Next let us go through a more detailed rating for this how this area would be determined in actual practice. Here are some additional design conditions:

Allowable pressure drop, tube side	10 psi
Allowable pressure drop, shell side	10 psi

We will plan to use an exchanger with ¾" OD tubes 20 ft. long, 14 BWG on a 1" square pitch. The shell baffles will be spaced every 12". To illustrate the calculations we will used a 2 shell pass, 4 tube pass exchanger. Some additional physical properties of the amines are:

	Lean Amine Shell Side	**Rich Amine Tube Side**
μ (viscosity in cp)	0.38	0.5
K (thermal cond.) BTU/hr/ft^2/°F/ft	0.312	0.312

The assumed overall fouling factor will be 0.0030.

The method of solution is to assume a number of tubes and thus the area, then find the overall heat transfer coefficient using the assumed number of tubes and then calculate the new area and see if this comes close to the assumed area. The overall coefficient U is found from the equation:

$$\frac{1}{U} = \frac{1}{h_0} + \frac{1}{h_i}\frac{D_0}{D_i} + R$$

h_O and h_i are found from the curves on Fig. 8 and Fig. 9-7 of the GPSA Data Book. These curves are based on the Sieder and Tate equation inside tubes:

$$\frac{h_i D_i}{K} = 0.027\left(\frac{DG}{\mu}\right)^{0.8}\left(\frac{C_P \mu}{K}\right)^{1/3}\left(\frac{\mu}{\mu_W}\right)^{0.14}$$

and by the Colburn equation for outside tubes:

$$\frac{H_0 D_e}{K} = 0.36\left(\frac{D_e G}{\mu}\right)^{0.55}\left(\frac{C_P \mu}{K}\right)^{1/3}\left(\frac{\mu}{\mu_W}\right)^{0.14}$$

These equations apply only over the turbulent flow range. Please note that the common symbols have been used above. In the GPSA Data Book slightly different symbols are used. Since we have a 2-4 exchanger we must correct the log mean temperature difference. This is done using the Figure 8-3 on page 8-3 of the GPSA Data Book.

$$P = \frac{210-140}{255-140} = 0.608$$

$$R = \frac{255-181}{210-140} = 1.051$$

$$\Delta T = F\Delta T_{LOG\ MEAN} = 0.89(43) = 38^0\ F$$

For a first try let us assume 700 tubes per pass. This gives an area of heat transfer of

700 (0.1963) (4) (20) = 11,000 ft^2

Let us first find h$_i$

$$G = \frac{1700(8.33)(1.02)(60)}{700\,\frac{0.2679}{144}} = 182 \quad lb/\sec.ft^2$$

G is the mass velocity

Now use Figure 9-7 in the GPSA Data Book.

$$N_R = \frac{DV}{Z} = \frac{0.584(182)}{0.5} = 213$$

J$_1$ = 1400 from curve

$$1400 = \left(\frac{h_i D_i}{K}\right)\left(\frac{CZ}{K}\right)^{-1/3}\frac{Z}{Z_W}$$

Ignore viscosity correction $\left(\frac{z}{z_W}\right)^{0.14}$

$$\frac{CZ}{K} = \frac{0.95(0.5)}{0.312} = 1.52$$

Solve for h$_i$

$$1400 = \frac{h_i(0.584)}{0.312}\frac{1}{1.15}$$

$$h_i = 852$$

Let us try the new method given in the GPSA Data Book in Section 8 of that manual. Let us for example calculate h$_i$. Use water as reference fluid.

$$r2 = fr1 = f(0.0009)$$

$$f = \left(\frac{\mu_2}{\mu_1}\right)^{0.47}\left(\frac{K_1}{K_2}\right)^{0.67}\left(\frac{C_{P1}}{C_{P2}}\right)^{0.33}\left(\frac{G_1}{G_2}\right)^{0.8}\left(\frac{D_{i2}}{D_{i1}}\right)^{0.2}$$

$$\left(\frac{\mu_2}{\mu_1}\right)^{0.47} = \left(\frac{0.5}{0.764}\right)^{0.47} = 0.819$$

$$\left(\frac{K_1}{K_2}\right)^{0.67} = \left(\frac{0.358}{0.312}\right)^{0.67} = 1.09$$

$$\left(\frac{C_{P1}}{C_{P2}}\right)^{0.33} = \left(\frac{1.0}{0.95}\right)^{0.33} = 1.016$$

$$\left(\frac{G_1}{G_2}\right)^{0.8} = \left(\frac{265}{182}\right)^{0.8} = 1.35$$

$$\left(\frac{D_{i2}}{D_{i1}}\right)^{0.2} = \left(\frac{0.62}{62}\right)^{0.2} = 1.0$$

$$r2 = 0.819(1.09)(1.016)(1.35)(0.0009) = 0.0011$$

$$h_i = \frac{1}{r} = 908$$

This checks close enough with previous values of h_i = 852.

Next let us find h_O. First must find G_m across tubes. Find cross sectional area across which flow occurs.

$$a_S = \frac{(Shell\ ID)(Opening\ between\ tubes)(BaffleSpacing)}{Pitch\ (144)}$$

Let us assume a 60" shell ID (This is actually obtained by a tube count).

$$a_S = \frac{60\left(\frac{1}{4}\right)(12)}{1(144)} = 1.25$$

Ignore longitudinal flow. Then

$$G_m = \frac{1600(8.33)(1.02)}{60(1.25)} = 181 \quad lbs/\sec .ft^2$$

Find h_O from Figure 8.8 in this section

$$N_S = \frac{D_0 G_m}{Z} = \frac{0.75(181)}{0.38} = 356$$

$$J_0 = 1800 = \frac{h_0 D_0}{K}\left(\frac{CZ}{K}\right)^{-1/3}$$

$$\frac{CZ}{K} = \frac{0.95(0.38)}{0.312} = 1.15$$

$$h_0 = \frac{1800(0.312)}{0.75(1.15)} = 715$$

We can now find U from the equation:

$$\frac{1}{U}=\frac{1}{h_0}+\frac{1}{h_i}\frac{D_0}{D_i}+R=\frac{1}{715}+\frac{1}{852}(1.284)+0.0030=0.0057$$

So U=170

Now check again using 500 tubes. This gives an area for heat transfer of 500(0.1963) (4) (20) = 7850.

Find new h_i. Find new G_m and new J_i factor (600 in this case)

h_i = 974

Similarly find h_O. We have assumed a much smaller shell.

Find j_O = 2000 and h_O = 878.

$$\frac{1}{U}=\frac{1}{878}+\frac{1}{874}(1.284)+0.0030=0.0054$$

So U = 185

$$Area=\frac{57{,}000{,}000}{184(38)}=8160\ ft^2$$

This is close enough. You should now check pressure drop in shell and tubes. We will find it is OK.

Table 8.5: Fouling Factors

Fouling Resistances for Water				
Temperature of Heating Medium	**Up to 240°F**		**240°F - 400°F***	
Temperature of Water	**125°For Less**		**Over 125°F**	
	Water Velocity Ft./Sec.		**Water Velocity Ft./Sec.**	
Types of Water	**3 Ft. And Less**	**Over 3 Ft.**	**3 Ft. And Less**	**Over 3 Ft.**
Sea Water	.005	.001	.001	.001
Brackish Water	.002	.001	.003	.002
Cooling Tower and Artificial Spray Pond				
Treated Makeup	.001	.001	.002	.002
Untreated	.003	.003	.005	.004
City of Well Water (i.e. Great Lakes)	.001	.001	.002	.002
Great Lakes	.001	.001	.002	.002
River Water				
Minimum	.002	.001	.003	.002
Mississippi	.003	.002	.004	.003
Delaware, Schuylkill	.003	.002	.004	.003
East River and New York Bay	.003	.002	.004	.003
Chicago Sanitary Canal	.008	.006	.010	.008

Muddy or Silty	.003	.002	.004	.003
Hard (Over 15 grains/gal.)	.003	.003	.005	.005
Engine Jacket	.001	.001	.001	.001
Distilled	.0005	.0005	.0005	.0005
Treated Boiler Feedwater	.001	.0005	.001	.001
Boiler Blowdown	.002	.002	.002	.002

* Ratings in columns 3 and 4 are based on a temperature of the heating medium of 240° - 400°F. If the heating medium temperature is over 400°F and the cooling medium is known to scale, these ratings should be modified accordingly.

Fouling Resistances for Industrial Fluids	
Oils	
Fuel Oil	.005
Transformer Oil	.001
Engine Lube Oil	.001
Quench Oil	.004
Gases and Vapors	
Manufactured Gas	.01
Engine Exhaust Gas	.01
Steam (nonoil bearing)	.0005
Exhaust Steam (oil bearing)	.001
Refrigerant Vapors	.002
Compressed Air	.002
Industrial Organic Heat Transfer Media	.001
Liquids	
Refrigerant	.001
Hydraulic Fluid	.001
Industrial Organic Heat Transfer Media	.001
Molten Heat Transfer Salts	.0005
Fouling Resistances for Chemical Processing Streams	
Gases and Vapors	
Acid Gas	.001
Solvent Vapors	.001
Stable Overhead Products	.001
Liquids	
MBA & DEA Solutions	.002
DEG & TEG Solutions	.002
Stable Side Draw and Bottom Product	.001
Caustic Solutions	.002
Vegetable Oils	.003
Fouling Resistances for Natural Gas-Gasoline Processing Streams	
Gases and Vapors	

Natural Gas	.001
Overhead Products	.001
Liquids	
Lean Oil	.002
Rich Oil	.001
Natural Gasoline & Liquefied Petroleum Gases	.001
Fouling Resistances for Oil Reginery Streams	
Crude & Vacuum Unit Gases and Vapors	
Atmospheric Tower Overhead Vapors Light Naphthas	.001
Vacuum Overhead Vapors	.002

Crude & Vacuum Liquids						
Crude Oil	**0°F-199°F**			**200°F-299°F**		
	Velocity Ft./Sec.			**Velocity Ft./Sec.**		
	Under 2 Ft.	**2-4 Ft.**	**4 Ft. and Over**	**Under 2 Ft.**	**2-4 Ft.**	**4 Ft. and Over**
Dry	.003	.002	.002	.003	.002	.002
Salt *	.003	.002	.002	.005	.004	.004
	300°F-499°F			**500°F and Over**		
	Velocity Ft./Sec.			**Velocity Ft./Sec.**		
	Under 2 Ft.	**2-4 Ft.**	**4 Ft. and Over**	**Under 2 Ft.**	**2-4 Ft.**	**4 Ft. and Over**
Dry	.004	.003	.002	.005	.004	.003
Salt *	.006	.005	.004	.007	.006	.005

* Normally desalted below this temperature range. (Asterisk to apply to 200°F-299°F, 300°F-499°F, 500°F and over).

Gasoline	.001
Naptha & Light Distillates	.001
Kerosene	.001
Light Gas Oil	.002
Heavy Gas Oil	.003
Heavy Fuel Oils	.005
Asphalt & Residuum	.010
Cracking & Coking Unit Streams	
Overhead Vapors	.002
Light Cycle Oil	.002
Heavy Cycle Oil	.003
Light Coker Gas Oil	.003
Heavy Coker Gas Oil	.004
Bottoms Slurry Oil (4½ ft./sec. minimum)	.003
Light Liquid Products	.002
Catalytic Reforming, Hydrocracking & Hydrodesulfurization Streams	
Reformer Charge	.002
Reformer Effluent	.001

Hydrocracker Charge & Effluent **	.002
Recycle Gas	.001
Hydrodesulfurization Charge & Effluent **	.002
Overhead Vapors	.001
Liquid Product over 50° A.P.I.	.001
Liquid Product 30° - 50° A.P.I.	.002

** Depending on charge characteristics and storage history, charge resistance may be many times this value.

Light Ends Processing Streams	
Overhead Vapors & Gases	.001
Liquid Products	.001
Absorption Oils	.002
Alkylation Trace Acid Streams	.002
Reboiler Streams	.003

8.6 Example Problems

Example Problem 8.2

The following mix is the feed to a substitute gas plant. It is supplied to the plant as a liquid at 20,000 BPD, at 500 psia and saturated.

Comp.	Mole %
C_2	20.5
C_3	10.5
iC_4	8.5
nC_4	11.5
iC_5	13.6
nC_5	14.3
C_{6+}	21.1

It is necessary to vaporize the mix so that it can be fed to a desulphurize reactor which operates only in the vapour phase.

It is planned to use the convection section of a fired heater for this service. The flue gas will enter the convection section at 900°F and exit at 450°F.

Determine the amount of square feet of convection section heat transfer surface required. Assume 2"00 bare schedule 80 pipe is used.

Assumptions:

a) hc for inside tubes = 120 .

b) ho outside tubes = 50 .

c) Use a Pk of 2,000 for any calculations.

d) Flow is single pass in the convection hydrocarbon section.

e) Use fouling factors .001 for both sides.

Example Problem 8.3

Determine the square feet of condensing surface required for totally condensing the following mixture from the top of a depentanizer.

Comp.	Mole %
nC_4	5.0
iC_5	35.5
nC_5	45.0
C_{6+}	14.5

The condenser duty is 30,000,000 BTU's/hr.

The condensing film heat transfer coefficient is 225 BTU's/hr ft^2 °F. Water from the Bow River is to be used. Assume that this water has a minimum fouling factor for river water. The water design inlet temperature is 60°F and the outlet temperature is 90°F.

The condenser operates at 100 psia.

The tubes used in the condenser are ¾”, i.e. 0.75” OD and 0.584" ID.

The heat transfer coefficient for turbulent water flow is 250 2o BTU's/hr ft^2 °F.

Example Problem 8.4

You are to determine the area of the convection tubes in a furnace in which the fluid in the tubes is Boiler feed water feeding a boiler that produces steam at 195 psia. The water is fed to convection section at 200°F and 205 psia. The specific heat of liquid water in range under consideration is 0.88 BTU/lb/°F.

The flue gases enter the convection section at 1500°F and leave at 500°F. The furnace has a duty of 10,000,000 BTU's/hr input. The furnace is 80% efficient assuming fuel is measured as net heating value. Also assume the fuel is pure methane and is fired with 20% excess air.

Data:

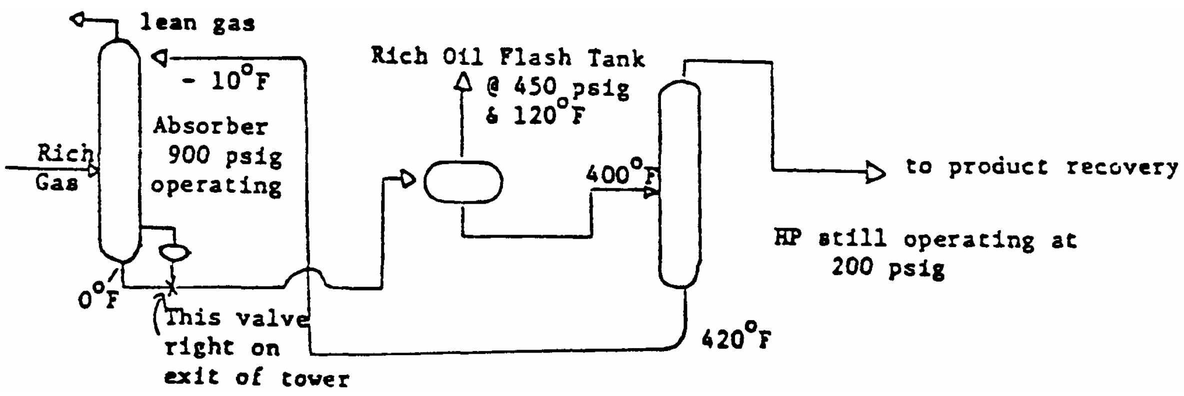
a) The specific heat of flue gas is 0.3 BTU/lb/°F

b) The flow of Boiler feed water is 15 USGM measured at 60°F.

c) The overall "U" for heat transfer is 20 BTU's/hr/ft^2 of bare tube surface.

Example Problem 8.5

You are to design the heat exchange system for a simple absorption oil system. The sketch below shows the system without the heat exchangers.



The lean oil is a 140 MW, 700 API oil and is circulated at the rate of 250 US gpm. Gas of the composition given below flows at a rate of 200 MMSCFD to the absorber.

Comp.	Mole %
C_1	84.0
C_2	7.8
C_3	2.2
iC_4	0.6
nC_4	1.0
iC_5	1.2
nC_5	1.8

Assume the following overall heat transfer coefficients.

		BTU/ft/sq.ft./°F
Lean Oil	Rich Oil	80
Lean Oil	Propane Refrigerant	110
Lean Oil	Cooling Water	100
Rich Oil	Exhaust Steam	130
Rich Oil	Fired Heater	80 * (assumed "U")

Assume Firebox equivalent temperature of 1000°F.

The cooling water available is at 60°F and can be raised to 90°F in the exchanger. The exhaust steam available is 55 psig and saturated.

Assume the following costs for exchangers (installed).

		$\$/\text{ft}^2$ of surface
Lean Oil	Rich Oil	8
Lean Oil	Propane	10
Lean Oil	Water	7
Rich Oil	Exhaust Steam	6
Rich Oil	Fired Heater	30

Determine the exchangers to use in the circuit by the minimum installed costs for exchangers.

For any calculations using "K" assume a Pk of 4000 and if needed assume lean oil has same "K" as decane. For simplification, assume that the specific heat of lean oil over the whole range of temperature is 0.60 BTU/HR/LB and the specific heat of rich oil over the whole range of temperature and process conditions 0.65 BTU/LB/HR.

Assume that 5 wt % of the rich oil flashes when passing through the let down valve from the absorber and that the heat of flashing is 100 BTU/LB.

Also assume an 80% C^3 absorption and essentially 100 C_{4+} absorption.

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9.0 Chemical Kinetics

- A review of the types of reactions.
- A preliminary discussion of the design of reaction vessels for chemical reactions.

9.1 Introduction

In handling natural gas and its associated products we are concerned with physical laws for the most part. Occasionally, however, there are chemical reactions taking place and in order to deal with these a knowledge of the chemical kinetics of the system is necessary. Chemical kinetics is a study of the rates and mechanisms of reactions.

Good examples of reactions in which chemical kinetics should be considered are the reactions involved in the production of sulphur. In the recovery of this product it is necessary to burn the H_2S in the acid gases from the sweetening unit to form SO_2 and to react the SO_2 with the remaining H_2S to form elemental sulphur. The simplified equations representing this process are:

Equation 9-1

$$H_2S + \frac{3}{2}O_2 + SO_2 + H_2O$$

Equation 9-2

$$SO_2 + 2H_2S + 3S + 2H_2O$$

To get a better understanding of how this process works and how to design the reactor in which these reactions occur, a study of the chemical reactions and the rates at which they occur is necessary.

9.2 Chemical Reactions

Let's generalize and consider some simple chemical reactions. For example:

Equation 9-3

$$A + B \Leftrightarrow C + D$$

The arrows here indicate a state of dynamic equilibrium. The reaction is said to be at equilibrium when the rate of forward reaction

Equation 9-4

$$A + B \Rightarrow C + D$$

is occurring at the same rate as the reverse action

Equation 9-5

$$C + D \Rightarrow A + B$$

The law of Mass Action states that the rate of a chemical reaction is proportional to the molecular concentrations of the reactants with each concentration raised to power equal to the number of molecules of each species participating in the process.

Applying this law to the above elementary reaction one may write:

Equation 9-6

$$Rate\ (forward)\ =\ k_1\,[A]\,[B]$$

and

Equation 9-7

$$Rate\ (reverse)\ =\ k_2\,[C]\,[D]$$

When the rate of the forward reaction equals the rate of the reverse reaction, dynamic equilibrium (i.e. the reactions continue) is achieved. Therefore

Equation 9-8

$$k_1[A][B] = k_2[C][D]$$

or

Equation 9-9

$$\frac{k_1}{k_2} = K_{equilibrium} = \frac{[C][D]}{[A][B]}$$

The expression for the equilibrium constant K is normally written with the concentrations of the products in the numerator and those of the reactants in the denominator. The square bracket [ ] stands for "concentration of". In the equilibrium expression developed above the quantities in the square brackets are given in molar concentrations. In the C.G.S. system the units are gm.moles/litre while in the British Engineering units they are lb.moles/cubic foot.

If during a reaction one of the products is removed from the system, the rate of the reverse reaction is reduced because of the lower concentration of this material in the rate equation. As a result the forward reaction continues until all of the reactants are consumed.

This may happen if a product is a precipitate which settles out of solution or if a gas forms which boils out of a liquid.

For example, the following reaction goes to completion in an aqueous solution.

Equation 9-10

$$NaCl\ +\ AgNO_3\ \rightarrow\ AgCl\downarrow\ +\ NaNO_3$$

A reaction also could be in the gaseous state and from which one of the products is readily condensed and removed from the reaction. This happens in the case of sulphur production. Sulphur condenses out and the reaction tends towards completion. To determine whether a reaction will go under certain conditions we need to determine the free energy of each of the reactants and products under the proposed reaction conditions. From these values one can determine the change in free energy ΔF.

ΔF = the sum of Free Energies of the Products - the sum of Free Energies of the reactants.

By thermodynamics it is known that

Equation 9-11

$$\Delta F = -RT \ln K_{equilibrium}$$

If the ΔF for the reaction is larger in a negative sense, it means that $K_{equilibrium}$ will be large. Since the products are in the numerator of the expression, this means that the reaction will go strongly to completion and is likely to be a good commercial reaction. If the value of $K_{equilibrium}$ turns out to be very small, it means that the reaction has little tendency to go to give products and may have little chance of commercial success.

9.3 Catalysis

A catalyst may be defined as (a) a substance which causes a reaction to go under conditions at which it may not go in the absence of a catalyst or (b) a substance which increases the rate but is not consumed by the reaction. Many different catalysts are used in industry. Examples of a number of reactions which occur in the presence of catalysts are:

1. In the formation of SO_3 from SO_2 in air, V_2O_5 is used as a catalyst.

Equation 9-12

$$SO_2 + \frac{1}{2} O_2 \quad \rightarrow \left(\frac{V_2O_5}{450^0 C} \right) \rightarrow \quad SO_3$$

   This reaction may be followed by hydration to yield sulphuric acid.

2. In the cracking of heavy hydrocarbons of petroleum, lighter gasoline components are products. In this reaction natural clays and synthetic zeolites are used as catalysts.
3. In the alkylation of isobutylene with isobutane, HF is used as an acid catalyst.
4. In the production of sulphur as given by equation (2) Bauxite is the catalyst mostly used.

There are many other examples.

The function of a catalyst is either (a) to increase the rate of a chemical reaction or (b) to increase a particular reaction to proceed in preference to another. Both of these alternatives may occur. The mechanism of catalytic action is generally quite complex. However, in most gaseous reactions the catalyst is an adsorbent of one or more of the reactants and provides a site on which the reaction may take place. For gaseous catalytic reactions to occur, the following steps take place:

1. Diffusion of the reactant to the surface of the catalyst.
2. Diffusion into the pores of the catalyst.
3. Adsorption of reactants onto the surface.
4. Chemical reaction on the surface.
5. Desorption of the product from the surface.
6. Diffusion of the products out of the pores.
7. Diffusion from the exterior of the catalyst into the gas stream.

Any one of these steps may actually control the catalytic rate. It is thought that the catalyst permits the reaction to go more easily by permitting intermediate complexes to form which have lower "energy of activation" that is observed when the reaction is performed in the absence of a catalyst. To understand "energy of activation" let us consider the following energy diagrams which describe what happens when (a) exothermic and (b) endothermic reactions occur (Figure 9.1 and Figure 9.2).

The energy of activation is always positive and must be supplied to the reactant molecules before they can form the intermediate complex which can then decompose to yield the products.

The effect of a catalyst on a reaction is to reduce the height of the activation energy peak and thereby to permit the reaction to occur at lower temperatures. The effect of a catalyst can be seen in Figure 9.3.

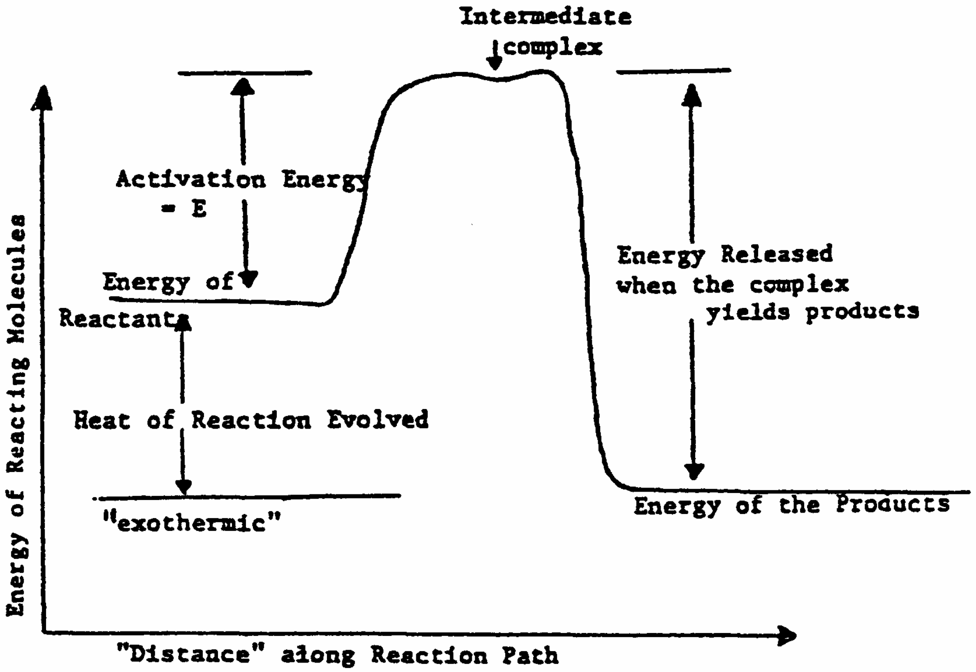


Figure 9.1: Exothermic Reaction

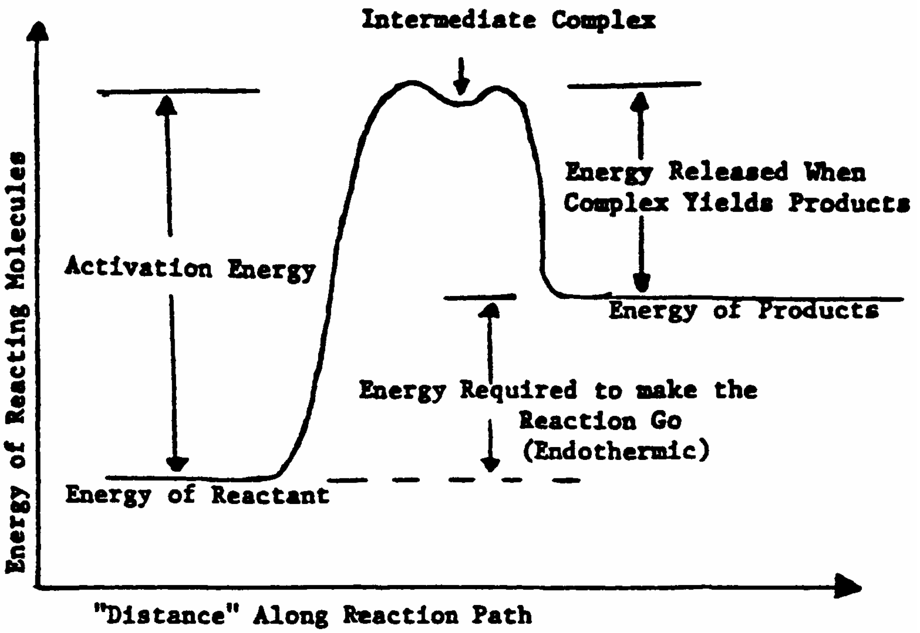


Figure 9.2: Endothermic Reaction

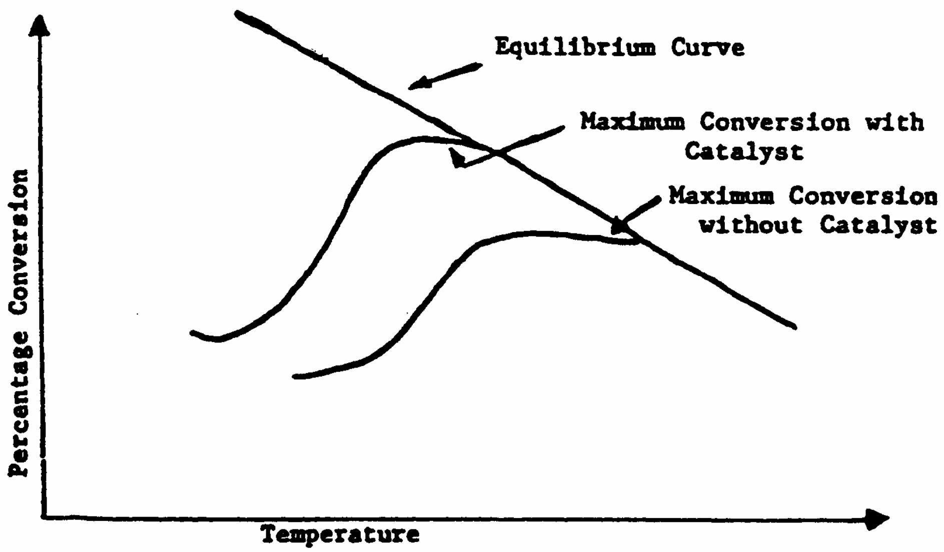


Figure 9.3: Effect of Catalyst on Reaction Rate

Figure 9.3 is for a reaction in which the equilibrium constant becomes less favorable as the temperature is increased.

9.4 Reaction Rates

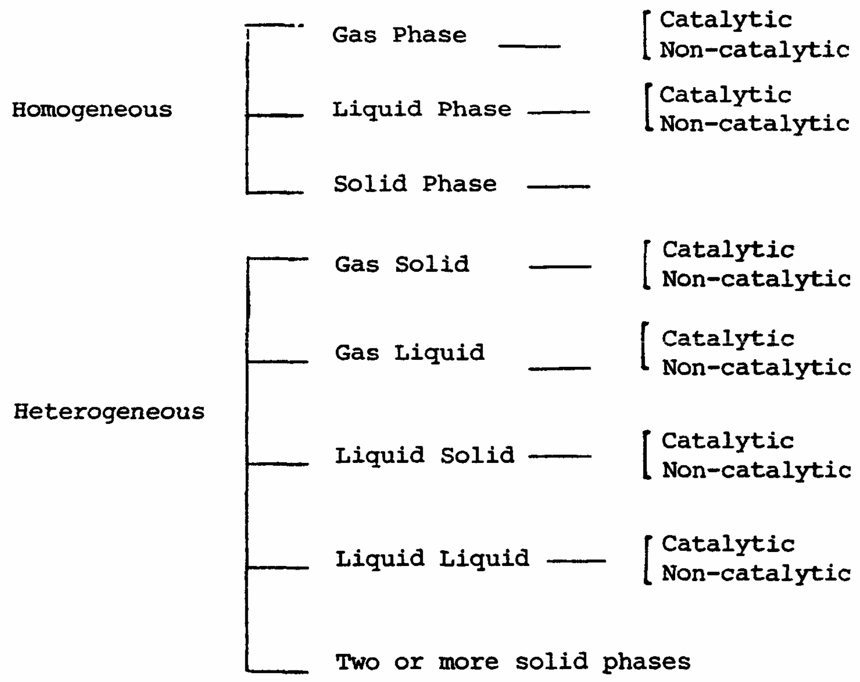
Reaction rate is equal to the change in the concentration of a reactant or product with time.

Equation 9-13

$$Rate = \frac{dc}{dt}$$

The rate is affected by (a) the concentration of the reactants, (b) the temperature, (c) the presence of catalysts and sometimes (d) diffusional or mass transfer processes.

9.4.1 Classification of Reactions



9.4.2 The Order of a Reaction

Consider the rate equation in which "r" is the rate

Equation 9-14

$$r = kC_A^a C_B^b$$

C_A and C_B are the concentrations of the reactants A and B. The power "a" and "b" give the order of the reaction with respect to A and B. The "overall order" of the reaction = a + b. The proportionality constant "k" is also known as the "specific rate constant".

If the reaction goes as indicated by the equation

Equation 9-15

$$aA + bB \rightarrow products$$

that is, if it is "elementary", then the powers “a" and "b" are the coefficients of A and B in the equation. If the reaction does not occur as this equation suggests, then the powers “a"and "b " need not be the same as the coefficients of the stoichiometric equation.

In order to determine the values of "a" and "b" in the kinetic rate expression, experimental work is required. Plots of some function of the concentration of the reactants are made versus time until a mathematical model is obtained which fits the data in the form of a straight line.

The order of a reaction may be 0, 1, 2, 3 or fractional. Consider the equation

Equation 9-16

$$A \rightarrow R + S$$

where:

rate "r" = kC_A

or

Equation 9-17

$$\frac{-dC_A}{dt} = kC_A$$

Here the negative sign means that the concentration of C_A is decreasing as the time "t" increases.

If one plots C_A versus "t" a curve as indicated in the sketch is obtained (Figure 9.4).

Such a curve does not reveal much. However, if the equation is integrated thus:

Equation 9-18

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k\int_0^t dt$$

one obtains:

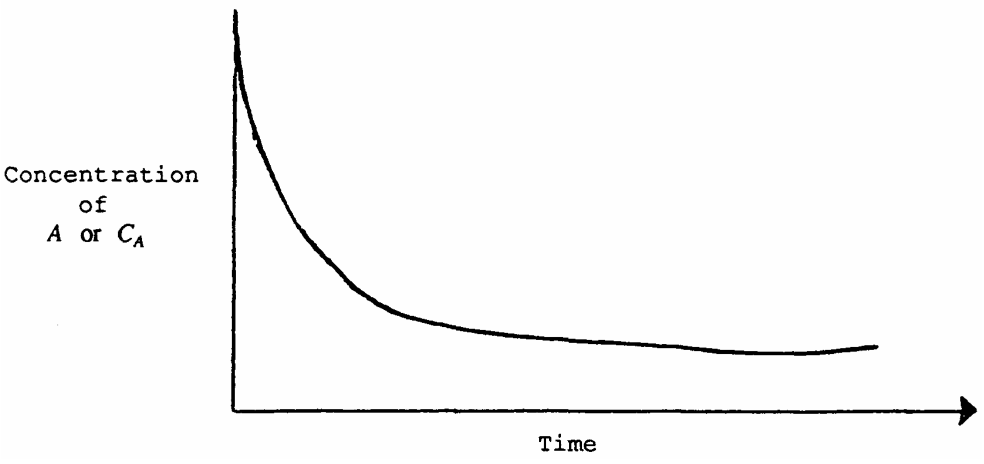


Figure 9.4: Concentration Vs Time

Equation 9-19

$$-\ln\frac{C_A}{C_{A0}} = kt$$

which may be rewritten as

Equation 9-20

$$\ln C_A = -kt + \ln C_{A0}$$

and which is in the form of a linear equation $y = mx + b$.

If one plots lnC_A versus t, a straight line of slope equal to k is obtained when a first order reaction is being studied.

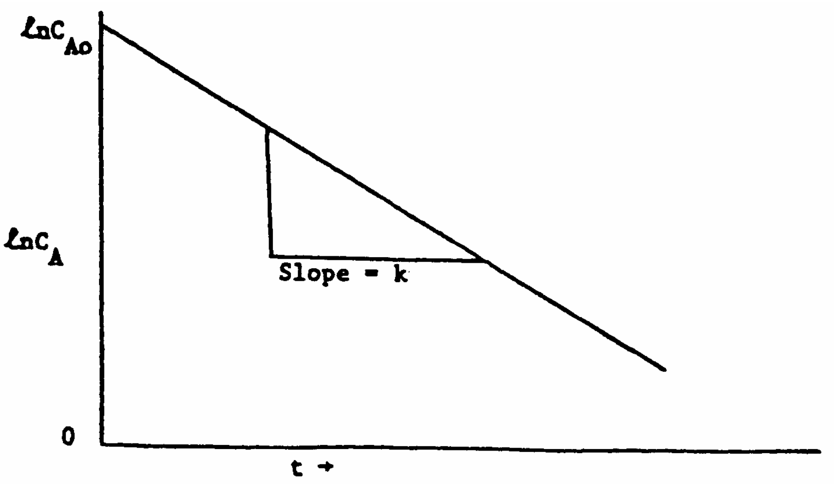


Figure 9.5: First Order Reaction

Proof that one is dealing with a first order reaction is provided if a straight line plot of the data is obtained.

For a second order reaction it is desirable to change the form of the expression and to let *x* be the number of moles of A or B converted. Consider the reaction

Equation 9-21

$$A + B \rightarrow 2P$$

Let w and y be the concentrations of A and B initially, then at time t

Equation 9-22

$$C_A = w - x$$

Equation 9-23

$$C_B = y - x$$

Upon integration by parts it can be shown that

Equation 9-24

$$\frac{1}{w-y}\ln\frac{y(w-x)}{w(y-x)}=kt$$

If the left hand side is plotted versus time and a straight line results, it may be concluded that the reaction is second order.

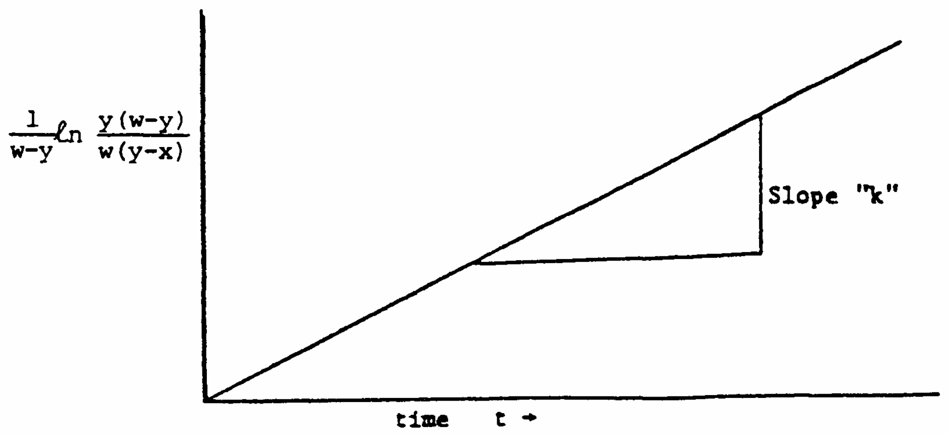


Figure 9.6: Second Order Reaction

Again the slope of the straight line yields the value of the rate constant k. There are other methods for handling third order and fractional order reactions. When a catalytic reaction is involved, the design work becomes complicated because you do not know which step controls. Pilot plant work is needed to determine experimentally which of the several possible controlling factors actually controls.

9.5 Reactor Process Design

9.5.1 Types of Reactors

Simple Batch

In the batch operation the reactants are loaded into the reactor initially, the reaction takes place and then the products are separated upon completion of the reaction.

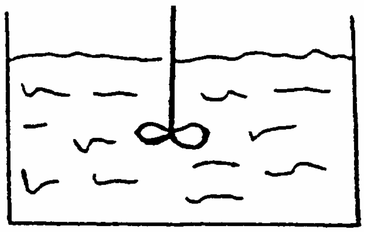


Figure 9.7: Batch Reactor

Semi-Batch

In semi-batch operation the reactants are fed and allowed to react for a set time.

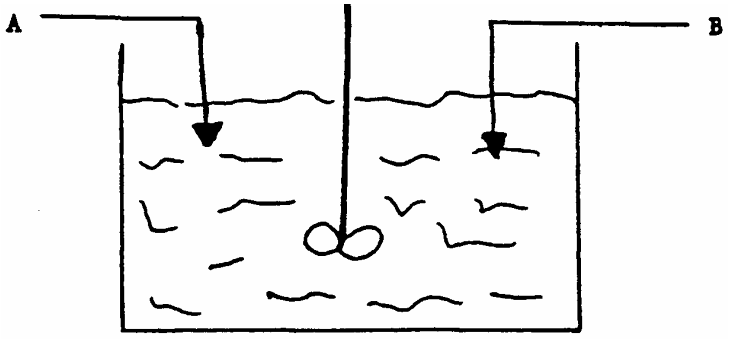


Figure 9.8: Semi-Batch Reactor

Continuous Stirred Tank Reactors

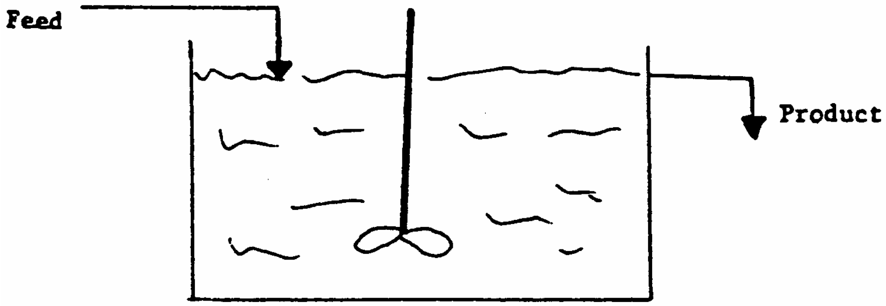


Figure 9.9: Continuous Stirred Tank Reactor

Feed is introduced and product taken of f continuously with this type of reactor.

Plug Flow Reactor

Figure 9.10: Plug Flow Reactor

This is essentially a pipe or tubular reactor. Feed is introduced and product removed continuously.

Most larger industrial processes are performed in continuous reactors whether the reaction is homogeneous or heterogeneous.

In reactor design work the terms $\frac{V_R}{F}$ and $\frac{W}{F}$ are often used.

where:

V_R = volume of the reactor.

F = flow rate in lbs/hr or cu.ft./hr (kg/hr or m^3/hr).

W = weight of catalyst.

The inverse of these terms, $\frac{F}{V_R}$ and $\frac{F}{W}$ is called "space velocity".

where:

$\frac{F}{V_R}$ = lbs feed/(hr)/(cu.ft. of reactor volume) or can be CF of flow/CF of Reactor Volume generally work out to be reciprocal hour as shown next or in the equivalent metric units of flow and volume.

$\frac{F}{W}$ = lbs feed/(hr) (lb of catalyst) = $\frac{1}{hr}$

If laboratory work indicates that a high space velocity is permissible it means that a smaller plant scale reactor may be used. If a low space velocity is required, the reactor must be large to get much throughput.

Let us consider a flow reactor and develop an equation for use in design.

$$F_{AO} = Feed\ of\ A/hr$$

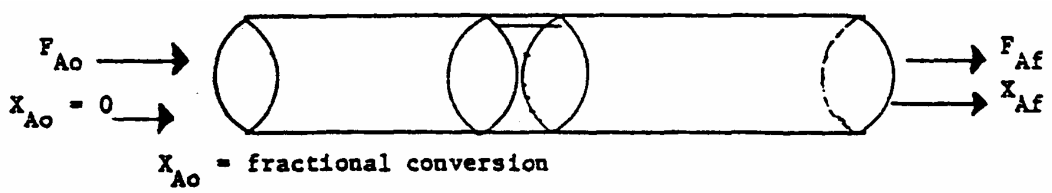


Figure 9.11: Flow Reactor - Fractional Conversion

Disappearance of A in the reaction section is

Equation 9-25

$$-r_A dv = \frac{moles\ of\ A\ reacting}{(time)(volume\ of\ reacting\ fluid)} x\ volume\ of\ fluid\ in\ segment\ considered$$

9.5.2 Material Balance

Input = Output + disappearance by reaction

Equation 9-26

$$F_A = (F_A + dF_A) + (-r_A)dv$$

Now, since (1-X_A) is the unconverted fraction

Equation 9-27

$$F_A = F_{A0}(1 - X_A)$$

Equation 9-28

$$dF_A = d(F_{A0}(1 - X_A)) = -F_{A0}dX_A$$

Therefore

Equation 9-29

$$F_{A0}dX_A = (-r_A)dv$$

This equation accounts for the small fraction of A converted in the section dv of the reactor.

Rearranging the equation and integrating:

Equation 9-30

$$\int_0^{V_R} \frac{dv}{F_{A0}} = \int_{X_{A0}}^{X_{Af}} \frac{dX_A}{-r_A}$$

Equation 9-31

$$\frac{V_R}{F_{A0}} = \int_{X_{A0}}^{X_{Af}} \frac{dX_A}{-r_A}$$

the design equation, where:

X = the fractional conversion of the feed.

V_R = the reactor volume.

$-r_A$ = the reaction rate which is a function of the reactant concentrations.

F_{AO} = the feed rate in lbs/hr or cu.ft./hr etc.

For catalytic reactors the design equation becomes:

Equation 9-32

$$\frac{W}{F_{A0}} = \int_{X_{A0}}^{X_{Af}} \frac{dX_A}{-r_A}$$

where:

W = the weight of the catalyst used.

Knowing the conversion required, the feed rate, and the reaction rate, r_A , one can calculate the volume of reactor or the weight of catalyst required.

Sometimes the reaction rate, r_A , is not known. Instead of determining it you may plot conversion versus reciprocal space velocity, as shown below.

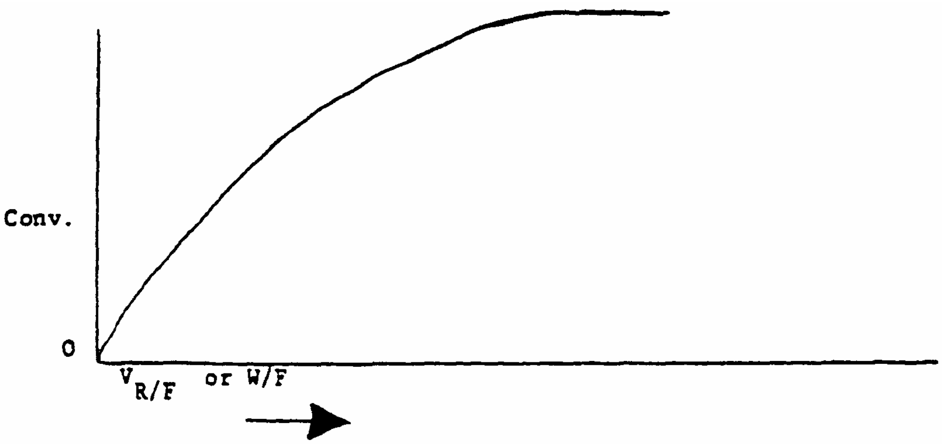


Figure 9.12: Conversion Versus Reciprocal Space Velocity

From the curve for a specific conversion X, one can calculate V_R or W for a given feed rate F.

In common reactions the space velocity has been determined. For example, for sulphur production the common value of space velocities used are 700 to 900 $\frac{\text{cu.ft./hr of flow}}{\text{cu.ft. catalyst}}$ or 1/hr. This is based on the total volume of gas feed to the reactor.

9.6 Sulphur Plants

This has been an elementary treatise on reaction kinetics. Let's follow through the design of a sulphur plant reaction system to see the considerations that are involved in the design of such a system.

The reactions involved are:

Reaction Furnace

Equation 9-33

$$H_2S + {}^3\!/_2\, O_2 \rightarrow H_2O + SO_2$$

$$\Delta H = -124 \; to \; 138 \quad kcal$$

Reactor

Equation 9-34

$$2H_2S + SO_2 \rightarrow 2H_2O + {}^3\!/_e\, S_e$$

$$\Delta H = -21 \; to \; -35 \quad kcal$$

The term $\frac{3}{e}S_e$ is used because of the many forms of S in the vapour (i.e. S_2, S_6, S_8, are most prominent.)

The design of a reaction system of this process is quite complex. Some of the problems are:

1. The equilibrium reaction of (2) above is favoured at low temperatures 400°F to 500°F (205°C to 260°C)
2. There is considerable heat evolved from the reaction.
3. The condensation of liquid sulphur on the catalyst poisons it; therefore we must keep reaction above a dewpoint of 350°F. (176°C). Generally the temperature is kept above 425°F. (218°C)
4. The reaction equilibrium can be shifted to the right by removing one of the products.
5. There is some elemental sulphur formed by free flame conversion in the waste heat boiler.

Therefore the process has evolved as follows:

1. Partially burn the H_2S - according to equations (33), then cool the effluent gases through a waste heat recovery boiler and a sulphur condenser as shown in the figure below.

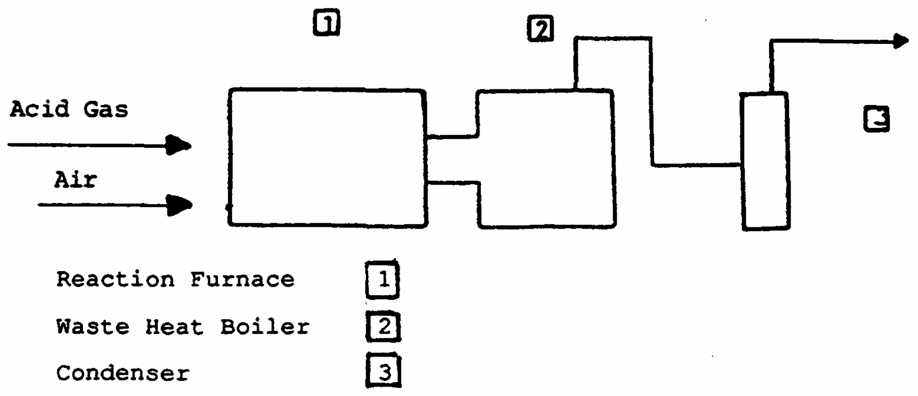


Figure 9.13: Start of a Sulphur Plant

2. Reheat the gases to about 450°F (232°C) and send to #1 converter.

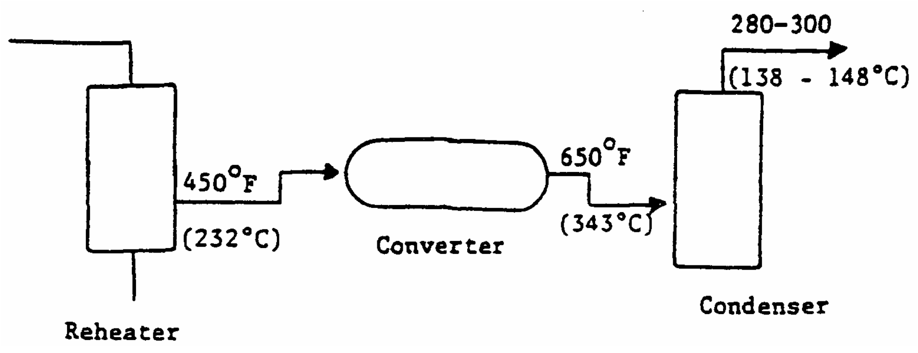


Figure 9.14: 1st Converter in a Sulphur Plant

Cool the gases from the reactor in a sulphur condenser.

3. Again reheat to 440°F (225°C) and send to the next converter.

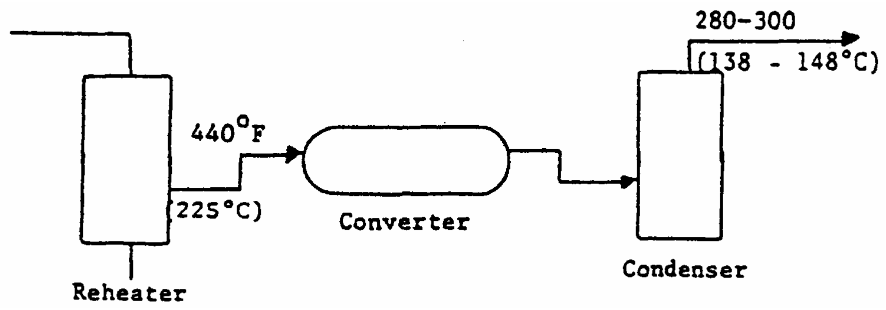


Figure 9.15: 2nd Converter in a Sulphur Plant

4. If further conversion is desired a further reheat and catalytic conversion step is carried out.

The condensers and reheaters are sized by common heat transfer calculations. The converters are sized by allowable space velocity. Normally the two converters are sized for the appropriate space velocity and the third is a backup. Because of governmental regulations on sulphur recoveries and discharges to the atmosphere, additional converters are often put in.

9.7 Example Problems

Example Problem 9.1

The graph attached shows the conversion of H_2S to element sulphur versus the reciprocal space velocity at specific pressure and at specific temperature range. Determine whether the two reactors sized for space velocities of 600 cu.ft. per hour/cu.ft. of catalyst or three reactors sized for space velocities of 1000 cu.ft. per hour/cu.ft. of catalyst.

Which system will give the greater % conversion?

- Assume complete removal of the sulphur after each converter.
- Assume that the % H_2S on the Y axis is based on the H_2S present in the feed to each reactor.

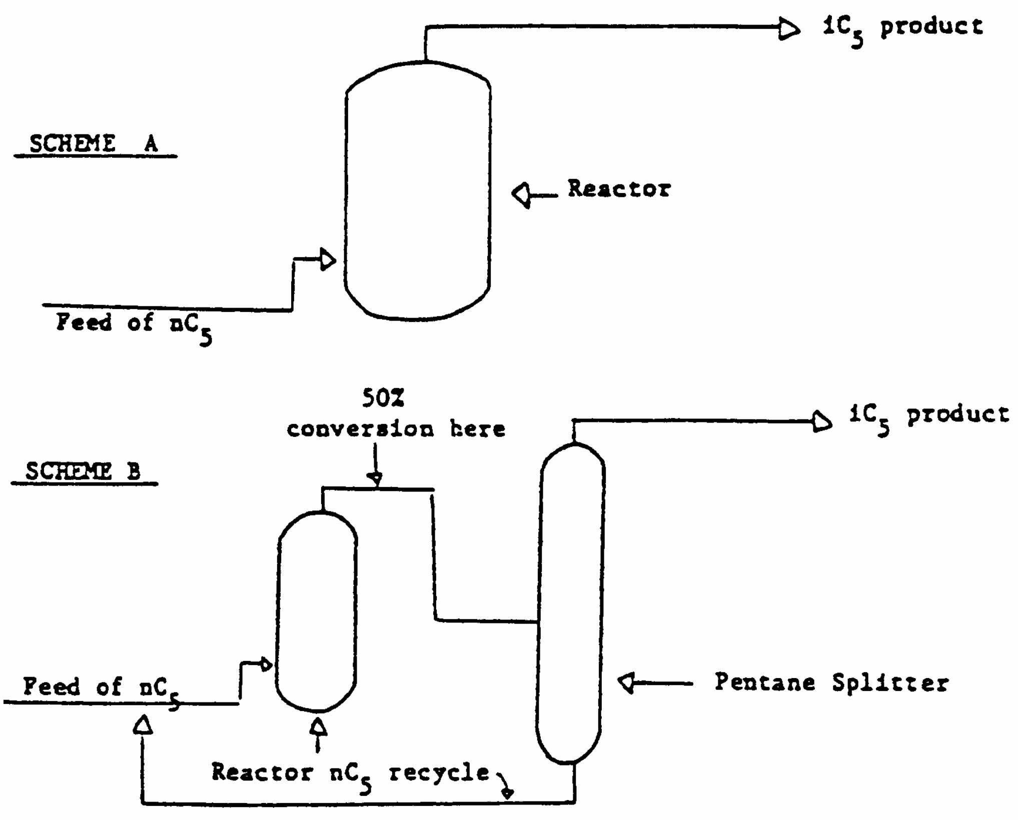
Example Problem 9.2

Isopentane is a very desirable high octane blending stock. Considerable amounts of it can be made by isomerizing n pentane. This process occurs by passing the n pentane through a reactor filled with a platinum catalyst. Below is listed the conversion data.

Mole % Converted of nC_5 iC_5	**Space Velocity** $\frac{\text{lbs/hr of feed}}{\text{lbs of Catalyst}}$
10	20.00
30	10.00
50	4.00
70	2.00
80	1.42
85	1.17
90	1.00
95	0.82

The production of n pentane is 5000 B/D and it is wished to produce an isopentane product containing 90 mole % iC_5.

Two possible schemes are proposed.



Determine which scheme you would use based on the lowest capital cost.

Data

- Reactor installed cost \$5.00/lb of catalyst needed.
- Pentane splitter 60¢/lb of feed/hr to it.
- Assume product leaving the pentane splitter is fractionated so as to produce a 90% iC_5 10% nC_5 stream and that the bottoms is a stream containing 90% nC_5 and 10% iC_5.
- Assume that the reaction gives a yield of a volume product for a volume feed and that it occurs in the liquid phase.
- For ease in calculation assume that both iso and normal pentane have a density of 5.2 lbs/US gallon.

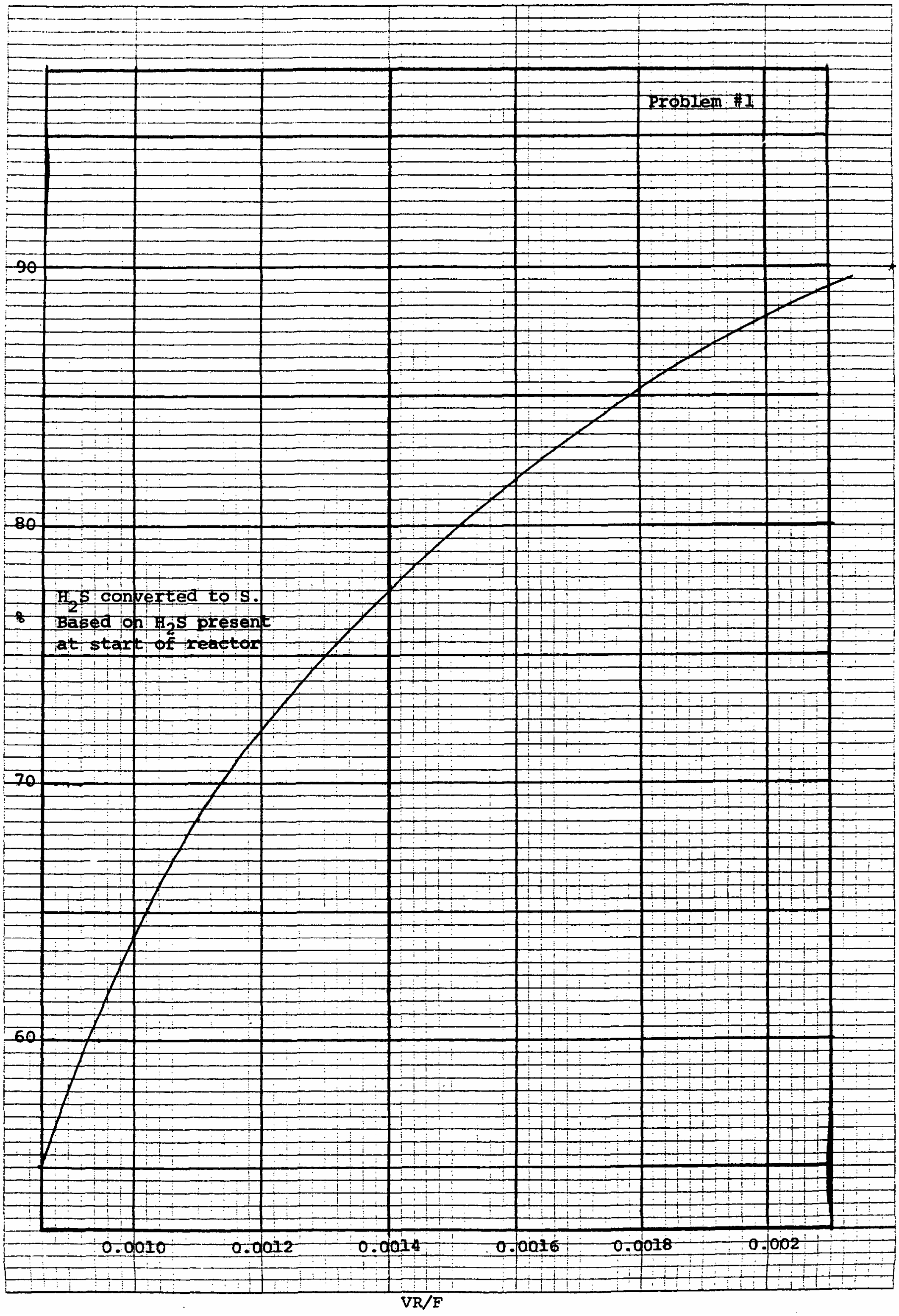


Figure 9.16: H_2S Converted to S

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Appendix 1.0 Natural Gas Processing Principles and Technology - Part I

List of Key Terms

List of Example Problems

List of Equations

Reference of Key Equations

$\left(P + \frac{a}{v^2}\right)(V - b) = RT$ 2-2

$P = \frac{RT}{V^2}\left(1 - \frac{c}{VT^3}\right)V + B_0\left(1 - \frac{b}{V}\right) - \frac{A_0}{V^2}\left(1 - \frac{a}{V}\right)$ 2-2

$P = RT\rho + \left(B_0RT - A - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4}\right)\rho^2 + \left(bRT - a - \frac{d}{T}\right)\rho^3 + \left(a + \frac{d}{T}\right)\alpha\rho^6 + \frac{c\rho^3}{T^2}\left(1 + \chi\rho^2\right)\exp\left(-\chi\rho^2\right)$
.... 2-3

$B_0 = \sum_i x_i B_{0i}$ 2-4

$b^{1/3} = \sum_i x_i b_i^{1/3}$ 2-4

$A_0 = \sum_i \sum_j \left(\frac{m_{ij}}{2}\right)^3 x_i x_j A_{0i}^{1/3} A_{0j}^{1/2}$ 2-4

$a^{1/3} = \sum_i x_i a_i^{1/3}$ 2-4

$C_0 = \sum_i \sum_j \left(\frac{m_{1j}}{2}\right)^3 x_i x_j C_{0i}^{1/2} C_{0j}^{1/2}$ 2-4

$\alpha^{1/3} = \sum_i x_i \alpha_i^{1/3}$ 2-4

$\chi^{1/2} = \sum_i x_i \chi_i^{1/2}$ 2-4

$c^{1/3} = \sum_i x_i c_i^{1/3}$ 2-4

$D_0 = \sum_i \sum_j \left(\frac{m_{ij}}{2}\right)^4 x_i x_j D_{0i}^{1/2} D_{0j}^{1/2}$ 2-4

$d^{1/3} = \sum_i x_i d_i^{1/3}$ 2-4

$P = \frac{RT}{V - b} - \frac{a}{T^{0.5}\, V\left(V + b\right)}$ 2-5

$Z = \frac{1}{1 - h} - \frac{A^2}{B}\left(\frac{h}{1 + h}\right)$ 2-5

$P = \frac{RT}{V - b} - \frac{a\left(T\right)}{V\left(V + b\right)}$ 2-5

$\Delta F^0 = RT \ln K$ 2-23

$\Delta F^0{}_{P-R} = \Delta H^0{}_{P-R} - T\Delta S^0{}_{P-R}$ 2-23

$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$ 2-24

$\left(\frac{\partial H}{\partial P}\right)_T = -\frac{RT^2}{P}\left(\frac{\partial Z}{\partial T}\right)_P$ 2-24

$H^0 - H = RT_C\left[\left(\frac{H^0 - H}{RT_C}\right)^0 + \varpi\left(\frac{H^0 - H}{RT_C}\right)\right]^1$ 2-24

$\mu = \left(\frac{\partial T}{\partial P}\right)_H$ 2-28

$H_{ideal} = \sum_i x_i H_i$ 2-29

$H_r = \frac{H_{ideal}}{Z}$ 2-29

$Z = 1 - \left(x_1\sqrt{b_1} + x_2\sqrt{b_2} + \ldots\ldots + x_n\sqrt{b_n}\right)^2$ 2-29

$\mu = \frac{Shearing\ Stress}{Rate\ of\ Shear\ Stress}$ 2-33

$\frac{k\ at\ high\ pressure}{k\ at\ atmospheric\ pressure}$ $from\ 16.29$ 2-36

$\sigma^{0.25} = \frac{P}{M}\left(d_1 - d_V\right)$ 2-36

$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$ 3-1

f(P,T,V) = 0..3-6

f(P,T,V,X) = 0 3-7

$K_i = \frac{y_i}{x_i}$ 4-1

$P_i = P_{VPi}\, x_i$ 4-2

$P_i = P_t\, y_i$ 4-2

$y_i P_t = P_{VPi}\, x_i$ 4-2

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$$x = \frac{\frac{zF}{L}}{K\frac{V}{L}+1} \text{ .... 4-20}$$

$$\sum_{i}^{n} x = 1.0 \text{ .... 4-20}$$

$$\sum_{i=1}^{n} x = \sum_{i=1}^{n} \frac{zF}{K\frac{V}{L}+1} = L \text{ .... 4-21}$$

$$W_{mixture} = Y_{HC}W_{HC} + Y_{H_2S}\, W_{H_2S} + Y_{CO_2}\, W_{CO_2} \text{ .... 5-3}$$

$$\overline{Pi} = HXi \text{ .... 5-7}$$

$$K_{v-s} = \frac{y}{x_s} \text{ .... 5-10}$$

$$\sum \frac{Y}{K} = 1.0 \text{ .... 5-10}$$

$$d = \frac{KW}{100M - MW} \text{ .... 5-15}$$

$$\mu = \frac{ShearingStress}{Rate\ of\ \ Shearing\ Strain} \text{ .... 6-2}$$

$$\frac{F}{A} = \mu\frac{dv}{dy} \quad or \quad = \mu\frac{d\gamma}{dt} \text{ .... 6-3}$$

$$\mathrm{Re} = \frac{(Diameter\ of\ Pipe)(Velocity\ of\ \ fluid)(Density\ of\ \ fluid)}{Vis\cos ity\ of\ \ fluid} = \frac{D\,v\,\rho}{\mu} \text{ .... 6-3}$$

$$F = \frac{f'\rho A\,v^2}{2g_c} \text{ .... 6-4}$$

$$u_2 + \frac{v_2^2}{2g_c} + z_2 + P_2V_2 = u_1 + \frac{v_1^2}{2g_c} + z_1 + P_1V_1 + q + w \text{ .... 6-5}$$

$$\Delta u + \Delta\left(\frac{v^2}{2g_c}\right) + \Delta z + PV = q + w \text{ .... 6-5}$$

$$\int_1^2 VdP + \Delta\left(\frac{v^2}{2g_c}\right) + \Delta z + lw \text{ .... 6-5}$$

$\frac{\Delta P}{\rho} + \Delta\left(\frac{v^2}{2g_c}\right) + \Delta z = lw$ 6-5

$F' = f'\frac{\rho\pi D L v^2}{2g_c}$ 6-6

$\frac{\rho\pi D^2 dL}{4}$ 6-6

$lw = \frac{F' dL}{\rho\pi D^2 dL \big/ 4} = \frac{4F'}{\rho\pi D^2}$ 6-6

$lw = \frac{2f'Lv^2}{Dg_c}$ 6-6

$lw = \frac{\Delta P}{\rho} = \frac{2f'Lv^2}{Dg_c}$ 6-6

Now let $f = 4f'$ $\quad f' = \frac{fm}{4}$ 6-6

$\Delta P = \frac{fm\rho Lv^2}{2g_c D} \qquad in\ lb \big/ ft^2$ 6-6

$\Delta P = \frac{\rho\, fm\, Lv^2}{144\, D(2g_c)}$ 6-7

$\Delta P = \frac{fW^2L}{5715\,\rho\, D^5}$ 6-10

$f = \frac{64}{\text{Re}}$ 6-10

Pv^k = Constant 6-15

$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^k$ 6-15

$k = \frac{C_P}{C_V}$ 6-15

$\frac{P_2}{P_1} = \frac{V_1}{V_2}$ 6-15

$P_1V_1 = U_2 - U_1 + \frac{v_2^2 - v_1^2}{2g_c} + P_2V_2$ 6-16

$C_V\left(T_2-T_1\right)=U_2-U_1$ 6-16

PV = RT..6-16

$C_V=\frac{R}{k-1}$ 6-16

$\frac{v_2^2-v_1^2}{2g_c}=P_1V_1-P_2V_2+C_V\left(T_1-T_2\right)$ 6-16

$\frac{v_2^2-v_1^2}{2g_c}=P_1V_1-P_2V_2+\frac{P_1V_1}{k-1}-\frac{P_2V_2}{k-1}$ 6-16

$\frac{v_2^2-v_1^2}{2g_c}=\frac{k}{k-1}\left(P_1V_1-P_2V_2\right)$ 6-16

$\frac{P_2}{P_1}=\left(\frac{V_1}{V_2}\right)^k=\left(\frac{\rho_2}{\rho_1}\right)^k$ 6-17

$\frac{v_2^2-v_1^2}{2g_c}=\left(\frac{k}{k-1}\right)\left(\frac{P_1}{\rho_1}\right)\left[1-\left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}\right]$ 6-17

$W=\frac{A_2v_2}{V_2}$ 6-17

$W=A\sqrt{\left(\frac{2kg_c}{k-1}\right)\left(\frac{P_1}{V_1}\right)\left(\frac{P_2}{P_1}\right)^{\frac{2}{k}}-\left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}}$ 6-17

$\frac{P_c}{P_1}=\left(\frac{2}{k+1}\right)^{\frac{1}{k-1}}$ 6-18

$v_c=\sqrt{\frac{2g_c}{k+1}k\left(P_1V_1\right)}=\sqrt{\frac{kP_c}{\rho_c}}$ 6-18

$v_c=\sqrt{kg_cT_c\frac{z_cR}{M}}$ 6-18

$VdP+\frac{d\left(v^2\right)}{2g_c}+dR=0$ 6-19

$dR=\frac{fv^2dl}{2g_cD}$ 6-19

$VdP + \frac{vdV}{g_c} + \frac{fv^2 dl}{2g_c D} = 0$ 6-19

$\frac{2g_c VdP}{v^2} + \frac{2dv}{v} + \frac{fdl}{D} = 0$ 6-19

$P_1^2 - P_2^2 = \frac{v_1^2 P_1}{g_c V_1}\left[2\ln\frac{v_2}{v_1} + \frac{fl}{D}\right]$ 6-19

$\frac{fl}{D} >> 2\ln\frac{v_2}{v_1}$ 6-19

$\frac{P_1^2 - P_2^2}{P_1^2} = \frac{flv_1^2}{g_c D_1 P_1 V_1}$ 6-19

$P_1 - P_2 = P_1\left[1 - \sqrt{1 - \frac{flv_1^2}{g_c DP_1 V_1}}\right]$ 6-20

$Q = K\frac{T_s}{P_s}\left[\frac{\left(P_1^2 - P_2^2\right)d^5}{fLSTZ_a}\right]^{\frac{1}{2}}$ 6-20

$f = \frac{0.032}{d^{\frac{1}{3}}}$ 6-22

$Q = 433.5\frac{T_b}{P_b}\left[\frac{P_1^2 - P_2^2}{STLZ_a}\right]^{\frac{1}{2}} d^{2.667}$ 6-22

$Q = 0.0037\frac{T_b}{P_b}\left[\frac{P_1^2 - P_2^2}{STLZ_a}\right]^{\frac{1}{2}} d^{2.667}$ 6-22

$\frac{1}{f} = \theta(\mathrm{Re})^{0.73}$ 6-23

$Q = KE\left(\frac{T_b}{P_b}\right)^{\alpha}\left(\frac{P_1^2 - P_2^2}{T_a LZ_a}\right)^{\beta}\frac{D^{\chi}}{S^{\nu}}$ 6-23

$P_1 = \left\{P_2^2 + K\left(\frac{Q}{E}\right)^{\alpha}\left(\frac{P_b}{T_b}\right)^{\beta}\frac{S^{\chi}}{D^{\nu}}T_a LZ_a\right\}^{1/2}$ 6-24

$P_2 = \left\{P_1^2 - K\left(\frac{Q}{E}\right)^{\alpha}\left(\frac{P_b}{T_b}\right)^{\beta}\frac{S^{\chi}}{D^{\nu}}T_a LZ_a\right\}^{1/2}$ 6-24

$$D = K\left(\frac{Q}{E}\right)^{\alpha}\left(\frac{P_b}{T_b}\right)^{\beta}\left(\frac{T_a L Z_a}{P_1^2 - P_2^2}\right)^{\chi}\frac{S}{1} \quad \ldots\ldots \text{6-24}$$

$$\frac{\Delta z\, S}{A T_a Z_a} = \frac{\ln P_1}{P_2} \quad \ldots\ldots \text{6-25}$$

$$\Delta P_{100} = \frac{W^2}{e}\left(\frac{0.000336\, f_f}{d^5}\right) \quad \ldots\ldots \text{6-25}$$

$$\frac{\Delta P}{100M} = \frac{W^2}{\rho}\left(\frac{62530\ x\ 10^2 f}{d^5}\right) \quad \ldots\ldots \text{6-26}$$

$$\Delta P_{total} = \Delta P_{two\ phase\ flow} + \Delta P_{elevation\ change} + \Delta P_{acceleration\ change} \quad \ldots\ldots \text{6-28}$$

$$\lambda = \left[\left(\frac{\rho_g}{0.075}\right)\left(\frac{\rho_L}{62.3}\right)\right]^{1/2} \quad \ldots\ldots \text{6-28}$$

$$\Psi = \frac{73}{\chi}\left[u_L\left(\frac{62.3}{\rho_L}\right)^2\right]^{1/3} \quad \ldots\ldots \text{6-29}$$

$$\Delta P_{TP} = \Delta P_G \phi_{GTT}^2 \quad \ldots\ldots \text{6-29}$$

$$\phi_{GTT} = \frac{14.2\, x^{0.75}}{L^{0.1}} \quad \ldots\ldots \text{6-30}$$

$$\phi_{GTT} = \frac{27.315\, x^{0.855}}{L^{0.17}} \quad \ldots\ldots \text{6-30}$$

$$\phi_{GTT} = \frac{15400\, x}{L^{0.8}} \quad \ldots\ldots \text{6-30}$$

$$\phi_{GTT} = \frac{1190\, x^{0.815}}{L^{0.5}} \quad \ldots\ldots \text{6-30}$$

$$\phi_{GTT} = (4.8 - 0.3125d)(X)^{0.343-0.021d} \quad \ldots\ldots \text{6-30}$$

$$x^2 = \left(\frac{\Delta P_{liquid}}{\Delta P_{gas}}\right) = \left(\frac{L}{G}\right)^{1.8}\left(\frac{\rho_g}{\rho_l}\right)\left(\frac{\mu_l}{\mu_g}\right)^{0.2} \quad \ldots\ldots \text{6-31}$$

$$\left(\frac{\mu_l}{\mu_g}\right)^{0.2} \approx 1.6 \quad \ldots\ldots \text{6-31}$$

$$x^2 = 1.6\left(\frac{L}{G}\right)^{1.8}\left(\frac{\rho_g}{\rho_l}\right) \quad \ldots\ldots \text{6-31}$$

$\Delta P_H = \dfrac{\sum h\, F_e\, \rho_L}{144}$ 6-41

$(\Delta P)_{increment} = \Delta P_f + (\Delta Z^+)\rho_M$ 6-42

$\rho_M = \rho_L\ E_L + \rho_G\,(1 - E_L)$ 6-42

U = $\dfrac{31{,}194\, Z\, Q}{Pd^2}$ in ft/sec.. 6-43

$U = \dfrac{31194(60)(0.800)}{(8)^2\,(1100)} = 21.3\ {}^{ft}\!/_{\sec}$ 6-44

$\Delta P_H = \dfrac{\rho_L\, F_e \sum h}{144} = \dfrac{44(0.12)(500)}{144} = 18.3\ psi$ 6-44

$\dfrac{U}{R^{0.32}} = \dfrac{21.3}{(12)^{0.32}} = 9.7$ 6-45

$Q = 435.87\, E \left(\dfrac{T_0}{P_0}\right)^{1.078} \left(\dfrac{P_1^2 - P_2^2}{L}\right)^{0.5394} \left(\dfrac{1}{T}\right)^{0.5394} \left(\dfrac{1}{G}\right)^{0.4606} \left(\dfrac{1}{Z}\right)^{0.5} d^{\,2.6182}$ 6-45

$60\,x10^6 = 435.87(0.86)\left(\dfrac{520}{14.65}\right)^{1.078} \left(\dfrac{1215^2 - P_2^2}{L}\right)^{0.5394} \left(\dfrac{1}{530}\right)^{0.5394} \left(\dfrac{1}{0.65}\right)^{0.4606} \left(\dfrac{1}{0.8}\right)^{0.5} 8^{2.6182}$ 6-45

$U = \dfrac{31194(60)(0.80)}{(10)^2\,(1100)} = 13.6\ {}^{ft}\!/_{\sec}$ 6-45

$\Delta P_H = \dfrac{44(0.18)(500)}{144} = 27.5\ psi$ 6-45

$\dfrac{U}{R^{0.32}} = \dfrac{13.6}{2.17} = 6.25$ 6-45

$60\,x10^6 = 435.87(0.77)\left(\dfrac{520}{14.65}\right)^{1.0781} \left(\dfrac{1215^2 - P_2^2}{10}\right)^{0.5394} \left(\dfrac{1}{530}\right)^{0.5394} \left(\dfrac{1}{0.65}\right)^{0.4606} \left(\dfrac{1}{0.80}\right)^{0.5} 10^{2.6182}$ P_2 =
1138 psi.. 6-45

$\dfrac{G}{\lambda}\ vs.\ \dfrac{L\lambda\Psi}{G}$ 6-46

$\Delta P_{two\ phase} = \phi_{GTT}^2\ \Delta P_G$ 6-46

$\lambda = \left[\left(\dfrac{\rho_G}{0.075}\right)\left(\dfrac{\rho_L}{62.3}\right)\right]^{1/2} = \left[\left(\dfrac{7.10}{0.075}\right)\left(\dfrac{44}{62.3}\right)\right]^{1/2} = 8.1$ 6-46

$Gas\ Flow\left(\frac{lb}{day}\right)=\frac{60\,x10^2}{384}(0.69)(29)=2.96\,x10^6\ {}^{lb}\!/_{day}$ 6-46

$G=\frac{2.96\,x10^6}{24\left(\frac{\pi}{4}\frac{10^2}{144}\right)}=226000\ \frac{{}^{lb}\!/_{hr}}{sq.ft.}$ 6-46

$\frac{G}{\lambda}=\frac{226000}{8.1}=28000$ 6-46

$\Psi=\frac{73}{\chi}\left[u_L\left(\frac{62.3}{\rho_L}\right)^2\right]^{1/3}$ 6-46

$\chi=22\,dynes/cm;\quad u_L=0.5$ 6-46

$\Psi=\frac{73}{22}\left[0.5\left(\frac{62.3}{44}\right)^2\right]^{1/3}=3.3$ 6-47

$L=\frac{12(60)(350)(0.7)(144)}{78.9(24)}=13200$ 6-47

$=\frac{13200}{226000}(8.1)(3.3)=1.56$ 6-47

$x^2=\left(\frac{13200}{226000}\right)^{1.8}\left(\frac{7.10}{44}\right)(1.6)=(0.058)^{1.8}(0.16)(1.6)=0.00152$ 6-47

$\phi^2=\frac{\Delta P_{TP}}{\Delta P_G}=1.2\qquad \Delta P_{TP}=0.2(1.2)=0.24$ 6-47

$\Delta P_{two\ phase}=0.24\ {}^{psi}\!/_{100\ foot\ of\ pipe}$ 6-47

$W=C_0\,A_0\sqrt{\frac{2g_c\rho(\Delta P)}{1-\left(\frac{A_0}{A_1}\right)^2}}$ 6-49

$Q=C\sqrt{h_w\,P_f}$ 6-49

$Q_h=C'\sqrt{h_w}$ 6-50

$Q_{TWE}=Q_{MP}\left(\frac{1+R_{HL}\,E}{1+R_{TL}\,S}\right)$ 6-50

NPSH = P_1 – VP + H_1 – H_2 - F..6-57

$\frac{C_P}{C_V} = K$ 6-58

$Y_{C_3} = Kx_{C_3}$ 7-2

$L_{n+1} + V_{n-1} = V_n + L_n$ 7-2

$J_A = -D_{AB}\frac{dC_A}{dZ}$ 7-4

$J_B = -D_{BA}\frac{dC_B}{dZ}$ 7-4

$C_A = \frac{P_A}{RT} \quad and \quad C_B = \frac{P_B}{RT}$ 7-4

$J_A = -\frac{D_{AB}}{RT}\frac{dP_A}{dZ}$ 7-5

$J_B = -\frac{D_{BA}}{RT}\frac{dP_B}{dZ}$ 7-5

$D_{1,2} = \frac{0.04381T^{1.5}\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^{0.5}}{p(\sigma_{1,2})^2\ \Omega_D}$ 7-5

$\frac{\varepsilon}{k} = 65.3T_C\, Z_C^{\ 3.6}$ 7-6

$\sigma = 0.7402\frac{(MV_C)^{0.333}}{z_C^{\ 1.2}}$ 7-6

$\sigma_{1,2} = \frac{1}{2}(\sigma_1 + \sigma_2)$ 7-6

$\frac{\varepsilon_{1,2}}{k} = \left[\left(\frac{\varepsilon_1}{k}\right)\left(\frac{\varepsilon_2}{k}\right)\right]^{0.5}$ 7-6

$D_{1,2} = \frac{1.59\,x10^{-7}(\Psi_2\ M_2)^{0.5T}}{\mu\left(\frac{M_1}{\rho_1}\right)^{0.6}}$ 7-7

$N_A = (N_A + N_B)\frac{P_A}{P} - \frac{D_{AB}}{RT}\frac{dP_A}{dZ}$ 7-8

$N_A = J_A = -N_B = -J_B$ 7-8

$y_{n+1} = \frac{R}{R+1} x_n + \frac{x_D}{R+1}$ 7-30

$\frac{\overline{L}}{\overline{V}} = \frac{\overline{L}}{\overline{L} - W}$ 7-31

$q = \frac{\overline{L} - L}{F} = \frac{H_V - H_F}{H_V - H_L}$ 7-31

$\frac{q}{q-1}$ 7-31

$y = \frac{q\,x}{q-1} - \frac{z_F}{q-1}$ 7-32

$\frac{q}{q-1} = 0$ 7-32

$\frac{q}{q-1} = \infty = \frac{1}{0}$ 7-32

$H_L = C_{PL}\left(t_L - t_0\right) M_{av} + D_S$ 7-33

$F = D + W$ 7-36

$F\,z_F = D\,y_D + W\,x_w$ 7-36

$\frac{D}{W} = \frac{z_F - x_w}{y_D - z_F}$ 7-36

$F\,H_F = D\,H_D + W\,H_W$ 7-36

$\frac{D}{W} = \frac{H_F - H_W}{H_D - H_F}$ 7-37

$\frac{D}{W} = \frac{z_F - x_w}{y_D - z_F} = \frac{H_F - H_W}{H_D - H_F}$ 7-37

$\frac{1}{slope} = \frac{y_D - z_F}{H_D - H_F} = \frac{z_F - x_w}{H_F - H_W} \quad \textit{with a common po}\mathrm{int}\ T$ 7-37

$\frac{Distillate}{Bottoms} = \frac{\overline{WF}}{FD}$ 7-37

$\frac{Bottoms}{Feed} = \frac{\overline{FD}}{WD}$ 7-38

$\frac{Distillate}{Feed} = \frac{\overline{F}\,\overline{W}}{WD}$ 7-38

$(1.74)^{SM} = \frac{(20.5)(6.7)}{(0.5)(0.3)} = 925 \qquad so\ SM = 12.3$ 7-49

$\log_{10}\left(\frac{Plates\ above\ feed}{Plates\ below\ feed}\right) = 0.206\log_{10}\left[\left(\frac{W}{D}\right)\left(\frac{Z_{HK}}{Z_{LK}}\right)\left(\frac{X_{LKW}}{X_{HLD}}\right)^{2}\right]$ 7-50

$E(overall\ efficiency) = \frac{n^{*}\ (number\ of\ theoretical\ trays)}{n\ (number\ of\ actual\ trays)}$ 7-50

$P_v = P_{vp}\, x$ 7-52

$P_v = m'\, x$ 7-53

$Y = \frac{moles\ solute}{moles\ inert\ carrier\ gas} \qquad and \qquad X = \frac{moles\ solute}{moles\ inert\ solvent\ in\ liquid}$ 7-53

$L_0\,(X_i - X_{i-1}) = V_{n+1}\,(Y_{i+1} - Y_i)$ 7-54

$y_i = \frac{Y_i\,(V_{n+1})}{V_i}$ 7-55

$x_i = \frac{X_i\,L_0}{L_i}$ 7-55

$y_i = K_i\, x_i$ 7-55

$Y_{i-1} = K_{i-1}\, x_{i-1}$ 7-56

$Y_i = K_i\,\frac{L_0}{L_i}\,\frac{V_i}{V_{n+1}}\,X_i$ 7-56

$Y_{i-1} = K_{i-1}\,\frac{L_0}{L_{i-1}}\,\frac{V_i}{V_{n+1}}\,X_{i-1}$ 7-56

$Y_i = \frac{Y_{i+1} + \frac{L_{i-1}}{K_{i-1}\,V_{i-1}}\,Y_{i-1}}{L + \frac{L_i}{K_i\,V_i}}$ 7-56

$Let \quad A = \frac{L}{KV} \quad or \quad A_i = \frac{L_i}{K_i\,V_i} \quad or \quad A_{i-1} = \frac{L_{i-1}}{K_{i-1}\,V_{i-1}}$ 7-56

$Y_i = \frac{Y_{i+1} + A_{i-1}\,Y_{i-1}}{L + A_i}$ 7-56

$$Absorption\ \% = \frac{Y_{n+1} - Y_1}{Y_{n+1} - Y_0} = \frac{A^{n+1} - A_0}{A^{n+1} - 1} \tag{7-56}$$

$$\frac{Y_{n+1} - Y_1}{Y_{n+1} - Y_0} \tag{7-57}$$

$$\frac{X_{m+1} - X_1}{X_{m+1} - X_0} = \frac{S^{m+1} - S}{S^{m+1} - 1} \tag{7-57}$$

$$V_i = V_1 \frac{n+1-i}{n} \tag{7-59}$$

$$\frac{V_i}{V_{i+1}} = \frac{V_1^{1/n}}{V_{n+1}} \tag{7-59}$$

$$L_i = L_0 + V_{i+1} - V_1 \tag{7-59}$$

$$\frac{T_n - T_i}{T_n - T_0} = \frac{V_{n+1} - V_{i+1}}{V_{n+1} - V_1} \tag{7-59}$$

$$A_e = \sqrt{A_n\left(A_1 + 1\right) + 0.25} - 0.5 \tag{7-59}$$

$$w_i = \alpha\left(p_i\right)^n \tag{7-62}$$

$$Rate = \frac{\text{driving force}}{\text{resistance}} \tag{8-1}$$

$$dQ = KA\frac{dt}{dx} \tag{8-1}$$

$$Q = \frac{K}{x}A(t_1 - t_2) \tag{8-1}$$

$$\mathrm{dQ = hAdt} \tag{8-2}$$

$$dQ = \sigma\varepsilon\, dA\, T^4 \tag{8-2}$$

$$Q_{12} = 0.173\, A_1\left[\varepsilon_1\left(\frac{T_1}{100}\right)^4 - \alpha_{12}\left(\frac{T_2}{100}\right)^4\right] \tag{8-3}$$

$$Q_{12} = 2.06\ x\ 10^7\ A_1\left[\varepsilon_1 T_1^{\,4} - \alpha_{12} T_2^{\,4}\right] \tag{8-3}$$

$$Q = UA\Delta T \tag{8-7}$$

$$Q = WC_P\left(T_1 - T_2\right) = W\left(H_1 - H_2\right) \tag{8-8}$$

$$\Delta T_{LMT} = \frac{\left(T_1 - t_2\right) - \left(T_2 - t_1\right)}{\ln\dfrac{T_1 - t_2}{T_2 - t_1}} \tag{8-8}$$

$h = 0.76\,K\left(\frac{g\rho_1^2}{\mu\Gamma}\right)^{1/3}$ 8-16

$\Gamma = \frac{W}{n\pi\frac{d}{12}}$ 8-17

$\Gamma = \frac{W}{2nL}$ 8-17

$\Gamma = \frac{W}{4n_r L}$ 8-17

$\left(\frac{Q}{A}\right)_{\max} = 143\,\rho_V\,\lambda\left(\frac{\rho_L - \rho_V}{\rho_V}\right)^{0.6}$ 8-19

$\left(t_S - t_b\right)_{\max} = \frac{1}{m}\left(\frac{Q}{A}\right)_{\max}$ 8-19

$\frac{h}{C_P G} = 4.02\left(\frac{DG}{\mu}\right)^{-0.3}\left(\frac{C_P\mu}{K}\right)^{-0.6}\left(\frac{P_L\chi}{p^2}\right)^{-0.425}\Sigma_L$ 8-20

$\frac{h\,d_r}{K_a(12)} = 0.1378\left(\frac{d_r G_m}{12\mu}\right)^{0.718}\left(\frac{C_P\mu}{K_a}\right)^{1/3}\left(\frac{S}{l}\right)^{0.296}F_r$ 8-20

$Q_{Rr} = \sigma\alpha A_{cp}F\left(T_g^4 - T_t^4\right)$ 8-21

$Q_{Rc} = h_{rc}A_{RT}\left(T_g - T_t\right)$ 8-21

$Q_{Rc} = 7.0\alpha A_{cp}\left(T_g - T_t\right)$ 8-22

$h_{cc} = \frac{2.14\left(T_f\right)^{0.28}\left(G_{\max}\right)^{0.6}}{d^{0.4}}$ 8-22

$Q = UA\frac{\left(T_1 - t\right) - \left(T_2 - t\right)}{\ln\frac{T_1 - t}{T_2 - t}}$ 8-28

$Q = WC_P\left(T_1 - T_2\right)$ 8-28

$Q = W\left(H_1 - H_2\right)$ 8-28

$H_2S + \frac{3}{2}O_2 + SO_2 + H_2O$ 9-1

$SO_2 + 2H_2S + 3S + 2H_2O$ 9-1