PROBLEM/SOLUTIONS

1. What is the mass of water in 1 m^3 of air having a temperature of 32°C and a relative humidity of 83%?

Solution

The partial pressure of water vapour $P_{v(H2O)}$ can be obtained from Figure 8.2, which is approximately 4.6 kPa at temperature = 305 K.

$$H_R / 100 \times P_{v(H2O)} = P_{actual(H2O)} \quad \text{(Section 8.1, near Table 8.1)}$$

$$0.83 \times 4.6 \text{ kPa} = 3.818 \text{ kPa}$$

$$3818 \text{ Pa} \times 1 \text{ m}^3 = n \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 305 \text{ K}$$

$$n = 1.5057 \text{ moles of water}$$

$$18.02 \text{ g mol}^{-1} \times 1.5057 \text{ mol} = 27.1 \text{ g of water}$$

2. Use Equation 8.4 to show why the total flux of solar radiant energy is about 10^5 times greater than that from the Earth.

Solution

Equation 8.4 is $F = \sigma T^4$, where

F = flux (energy emitted, in this case, from 1 m^2 of Earth)
T = average temperature (K) of Earth, T = 290 K (see Table 8.2)
σ = Stefan-Boltzmann constant = 5.67×10^{-8} W m^{-2} K^{-4}

$$F = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \times 290^4 = 401 \text{ W m}^{-2}$$

The flux from the Earth is 401 W m^{-2}.

The solar flux can also be calculated. Assume the surface temperature of the Sun is 5800 K.

$$F = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \times 5800^4 = 6.42 \times 10^7 \text{ W m}^{-2}$$

Ratio of flux values solar flux : Earth flux

$$6.42\times10^7 \text{ W m}^{-2} \div 401 \text{ W m}^{-2} = 1.6 \times 10^5$$

From the calculations done above, it is clear that the solar flux is about 1.6 x 10^5 times greater than the flux from the Earth.

3. The average albedo of the Earth is 0.31. Consider the following components of the Earth's surface—oceans, rainforests, deserts. How would you expect their albedo to differ from the average?

Solution

The Earth's albedo is determined from the combination of all factors affecting the amount of light reaching the Earth, being absorbed and reflected. Given that we are looking only at the surface elements in this case, the atmospheric processes shown in Figure 8.4 would still likely occur to the same extent. That is, in the atmosphere 0.25 (0.07 + 0.18) would still be reflected in the same way, while 0.23 (0.19 + 0.04) would be absorbed. Thus, we will now only consider the remaining 0.52 that reaches the Earth's surface.

The oceans – would likely be similar to the average, 0.46 absorbed and 0.06 reflected for a total albedo of 0.31. (total reflected 0.25 (atmosphere) + 0.06 (ocean) = 0.31)

Rain forests – would likely absorb more strongly than 0.46, would be less reflective and the total albedo would be less than 0.31.

Deserts – would likely reflect more strongly than 0.46, would have a total albedo that was higher than 0.31.

One could argue that in the case of the desert, on average, there would be less cloud cover, and more than 0.52 would reach the ground. Specifically, more of the 0.17 reflected from the cloud cover would reach the surface. However, it is also likely that there would be more aerosol cover that would to some extent counteract this increase of radiation striking the surface. In any event, it is likely that the surface sands would strongly reflect and generate a higher albedo than 0.31.

4. The current concentration of carbon dioxide in the atmosphere is 402 ppmv. It was indicated in the text that annual anthropogenic additions to the atmosphere are about 8 Gt (as C) of which about 4 Gt are removed into oceans and the terrestrial environment. Use these numbers to estimate the yearly net increase in atmospheric carbon dioxide mixing ratio in ppmv.

Solution

1 Gt = 10^9 t, 1 t = 1000 kg, therefore 8 Gt = 8×10^{12} kg (Appendix C.2)

The current atmospheric mixing ratio of CO_2 = 402 ppmv

Assume all C added to the environment ends up as CO_2 (a reasonable assumption).

Net annual addition of carbon to the atmosphere equals C added minus C taken up by the oceans and the terrestrial environment

$$8 \times 10^{12} \text{ kg C} - 4 \times 10^{12} \text{ kg C} = 4 \times 10^{12} \text{ kg C}$$

The total amount of C already in the atmosphere can also be calculated.

The mass of total atmosphere is 5.27×10^{18} kg. The average molar mass of 'air' is 0.02896 kg mol^{-1} (Chapter 2, using Equation 2.2).

This gives a total number of moles of all gases in the atmosphere:

$$5.27 \times 10^{18} \text{ kg} \div 0.02896 \text{ kg mol}^{-1} = 1.82 \times 10^{20} \text{ mol}$$

The number of moles of CO_2 (or equivalent moles of C), calculated using the current CO_2 mixing ratio is

$$\frac{\text{mol } CO_2}{1.82 \times 10^{20} \text{ total mol}} \times 10^6 = 402 \text{ ppmv}$$

$$\text{moles of } CO_2 \text{ (or C)} = 7.32 \times 10^{16}$$

$$\text{Mass of C} = 7.32 \times 10^{16} \text{ mol} \times 0.012011 \text{ kg mol}^{-1} = 8.79 \times 10^{14} \text{ kg of C}$$

The total mass of C is the existing mass plus newly added C, from above:

$$8.79 \times 10^{14} \text{ kg C} + 4 \times 10^{12} \text{ kg C} = 8.83 \times 10^{14} \text{ kg C}$$

$$8.83 \times 10^{14} \text{ kg C} \div 0.012011 \text{ kg mol}^{-1} = 7.35 \times 10^{16} \text{ mol of C}$$

(or moles of CO_2) and assuming total number of moles is unaffected the new concentration of CO_2 is:

$$\frac{7.35 \times 10^{16}}{1.82 \times 10^{20}} \times 10^6 = 404 \text{ ppmv}$$

The yearly increase in atmospheric carbon dioxide mixing ratio (associated with anthropogenic additions) is predicted to be approximately 2 ppmv.

5. Express the amount (65 Mt) of carbon dioxide derived from the Kuwait fires in 1991 as a percentage of the total annual anthropogenic addition of the gas. Note, as indicated in the previous question, that the calculated increase in atmospheric carbon dioxide is only a fraction of what goes into the atmosphere.

Solution

$65 \text{ Mt} = 65 \times 10^6 \text{ t} = 6.5 \times 10^{10} \text{ kg } CO_2$ & $8 \text{ Gt} = 8 \times 10^{12} \text{ kg C}$

The net increase (anthropogenic) of C was 4 Gt.

This gives: $4 \times 10^{12} \text{ kg C} \div 0.012011 \text{ kg mol}^{-1} = 3.33 \times 10^{14}$ mol of C, or an equivalence number of moles of CO_2.

The mass of the anthropogenic CO_2 gas is then:

$$3.33 \times 10^{14} \text{ mol} \times 0.04401 \text{ kg mol}^{-1} = 1.47 \times 10^{13} \text{ kg}$$

Assume the same ratio of C from the Kuwait fires is taken up by the oceans and terrestrial environments i.e., half of the CO_2 will remain as a net gain in the atmosphere.

$$0.5 \times 6.5 \times 10^{10} \text{ kg } CO_2 = 3.25 \times 10^{10} \text{ kg } CO_2$$

$$\frac{3.25 \times 10^{10} \text{ kg } CO_2 \text{ from Kuwait fires}}{} \times 100\ \% = 0.22\ \%$$

1.47×10^{13} kg CO_2 total anthropogenic addition

The Kuwait fires accounted for approximately one quarter of one percent of the CO_2 emitted into the environment in the year 1991.

6. There has been a steady decrease in the ratio of ^{14}C to ^{12}C in the atmosphere over the past decade. Explain how this is consistent with the view that the well-documented increase in atmospheric carbon dioxide concentrations is primarily due to emissions from the combustion of fossil fuels.

Solution

Fossil fuel is a very 'old' fuel that requires many years to form (thousands of years). During this time carbon-14 will have been decaying to carbon-12, $t_{½}$ = 5730 y. The burning of this fuel will release CO_2 to the atmosphere that is disproportionately high in carbon-12 compared with more recently derived CO_2 from 'younger' carbon sources. A living carbon-based organism will replenish C continually and 'live' in a steady-state of a natural abundance of carbon-14, but once dead, no further uptake of carbon-14 is possible and the only on-going change will be carbon-14 decay. In essence, our use of 'old' fuel is 'diluting' the atmosphere with carbon-12, enhancing the rate of the decreasing ratio of ^{14}C to ^{12}C.

7. Estimates (Additional Resources 1) for emissions of methane to the atmosphere are given in the table below and the current atmospheric concentration is 1.834 ppmv. Calculate its residence time.

Sources of atmospheric methane	**Million tonnes per year**
Wetlands and other natural sources	160
Fossil fuel related sources	100
Other anthropogenic sources of biological origin	275

There may be 10^{14} t of methane hydrate ($CH_4 \cdot 6H_2O$) in the permafrost below the ocean floors. If 1% of this were to melt per year, what would be the increased concentration of methane (ppmv y^{-1}) in the atmosphere neglecting any removal processes. What sinks for methane would play a role in reducing this concentration?

Solution

Steady-state amount of methane in atmosphere:

$$\frac{\text{mol } CH_4}{\text{total mol in atmosphere}} = \frac{\text{mol } CH_4}{1.82 \times 10^{20}} \times 10^6 = 1.834 \text{ ppmv}$$

$$\text{mol } CH_4 = 3.34 \times 10^{14} \quad \text{(in atmosphere = steady-state amount)}$$

Steady-state mass of methane in atmosphere is:

$$3.34 \times 10^{14} \text{ mol} \times 0.016043 \text{ kg mol}^{-1} = 5.35 \times 10^{12} \text{ kg } CH_4$$

From the table above, total methane flux into the atmosphere $= (160 + 100 + 275) \times 10^6 \text{ t y}^{-1}$

$$= 535 \times 10^6 \text{ t y}^{-1} = 5.35 \times 10^{11} \text{ kg y}^{-1}$$

$$\text{Residence time} = \frac{\text{Steady-state amount}}{\text{Flux in or out}} \qquad \text{(see Chapter 1, p.11)}$$

$$\text{Residence time} = \frac{5.35 \times 10^{12}\ \text{kg}\ \text{CH}_4}{5.35 \times 10^{11}\ \text{kg}\cdot\text{y}^{-1}} = 10\ \text{y}$$

If 1 % of the ice (containing methane hydrate) were to melt per year, it would release 1 % of the methane hydrate:

$$0.01 \times 10^{14}\ \text{t} = 1 \times 10^{12}\ \text{t} = 1 \times 10^{15}\ \text{kg of CH}_4\text{•6H}_2\text{O}$$

$$1 \times 10^{15}\ \text{kg} \div 0.12413\ \text{kg mol}^{-1} = 8.06 \times 10^{15}\ \text{mol of CH}_4\text{•6H}_2\text{O or CH}_4$$

$$8.06 \times 10^{15}\ \text{mol} \times 0.016043\ \text{kg mol}^{-1} = 1.29 \times 10^{14}\ \text{kg}\ \text{CH}_4$$

Total moles of CH_4 after 1% melt in one year is:

$$\underset{\text{(existing)}}{3.34 \times 10^{14}\ \text{mol}} + \underset{\text{(from hydrate)}}{8.06 \times 10^{15}\ \text{mol}} = 8.39 \times 10^{15}\ \text{mol of CH}_4$$

$$\frac{8.39 \times 10^{15}\ \text{mol of CH}_4}{1.82 \times 10^{20}} \times 10^{6} = 46\ \text{ppmv}$$

Without taking into account removal mechanisms, the increase in atmospheric methane concentration would be of the order of 46 ppmv per year for the melting of 1% per year of the trapped methane hydrate.

Removal process for methane:

Reaction of methane with the hydroxyl radical is a slow process (slowest of all hydrocarbon materials). But because methane is the most abundant of all hydrocarbons, the primary sink for methane is the reaction with the hydroxide radical, eventually forming formaldehyde or acetic acid. A second sink that could assist with the reduction of methane would be slow leakage into the stratosphere where it undergoes reaction with the excited singlet of oxygen $O(^1D)$ to generate hydroxyl radicals and ultimately CO.

8. Recent work[1] has shown that the flux of methane released from fens in the boreal forest area of Saskatchewan, Canada range from 176 to 2250 mmol $m^{-2}\ y^{-1}$. Daily fluxes range from 1.08 to 13.8 mmol $m^{-2}\ d^{-1}$. The data indicate that there are correlations between methane release and water depth (negative), water flow (negative), temperature (positive), and inorganic phosphorus in the sedimentary interstitial water (positive). Suggest reasons for these correlations.

Solution

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[1] Rask, H., D.W. Anderson, and J. Schoenau, Methane fluxes from boreal forest wetlands in Saskatchewan, Canada, *Can. J. Soil Sci.*, **76** (1996), 230.

Methane release from fens range from 176 mmol m^{-2} y^{-1} to 2250 mmol m^{-2} y^{-1} or from 1.08 mmol m^{-2} d^{-1} to 13.8 mmol m^{-2} d^{-1}.

Summary of relationships between methane release and:

i) water depth (negative)
ii) water flow (negative)
iii) temperature (positive)
iv) inorganic phosphorus in the sedimentary interstitial water (positive)

Refer to Section 8.3 - Methane

Water flow would be associated with conditions where 'less reducing' environments persist. With faster flowing water, there is increased contact between water and air leading to better aeration ('less reducing' conditions). Water depth would also lead to less reducing conditions since the total amount of water flowing would be greater, providing a larger supply of oxygen. In a larger volume of water, there is a larger amount of oxygen, so that a residual amount could be present after all the easily decomposable organic matter has been oxidized.

Temperature and inorganic P could be associated with growth conditions and the concomitant release of methane. Warmer temperatures and high availability of the limiting nutrient phosphorus would stimulate growth of the micro-organisms that oxidatively degrade organic matter, using up all the oxygen present in the water. Under the moist reducing conditions, methane production is favoured. The reactions leading to methane production are described in Chapter 15.

9. The Arrhenius parameters for the reaction

$$N_2O \rightarrow N_2 + O$$

are $A = 7.94 \times 10^{11}$ s^{-1} and $E_a = 250$ kJ mol^{-1}. The reaction is first-order. Calculate the rate constant and half-life of nitrous oxide assuming a tropospheric mixing ratio of 319 ppbv N_2O at 20ºC and comment on the environmental significance of these results.

Solution

A = 7.94 x 10^{11} s^{-1} and E_a = 250 kJ mol^{-1} (first order)
Calculate the rate constant and half-life of N_2O given 319 ppbv (20ºC)
Refer to Chapter 3 (Section 3.5, Kinetic calculations) for the Arrhenius equation.

$$k = Ae^{-Ea/RT}$$

$$\text{rate constant (k)} = 7.94 \times 10^{11}\ s^{-1}\ e^{-(250000\ /\ 8.315 \times 293)} = 2.13 \times 10^{-33}\ s^{-1}$$

$$t_{½} = \ln 2 \div k \qquad t_{½} = \ln 2 \div 2.13 \times 10^{-33}\ s^{-1}$$

$$t_{½} = 3.2 \times 10^{32}\ s\ \ (\sim 1 \times 10^{25}\ \text{years!})$$

The reaction $N_2O \rightarrow N_2 + O$ will be exceedingly slow (k = 2.13 x 10^{-33} s^{-1}) and will not be an efficient means of destroying N_2O in the troposphere. The residence time in the troposphere is long – about 120 years - but not nearly as long as our calculation suggests. Other removal processes must be occurring or the nitrous oxide level in the troposphere would be rising at a very rapid rate. One removal process is leakage into the stratosphere. It is destroyed there by reaction with ozone as we have seen in Chapter 3. As well, N_2O will act as a greenhouse gas while it is present in the troposphere.

10. Discuss the possible effects of the following on greenhouse gas chemistry.

(a) The southern Pacific Ocean is seeded with the algal micronutrients zinc and iron;

(b) CFCs cause further thinning of the ozone layer in the stratosphere;

(c) Urban air pollution leads to increased tropospheric ozone concentrations;

(d) Rice (paddy) is grown, under submerged conditions, on coarse sandy soils, rather than on fine clay-rich soils.

Solution

Greenhouse gas chemistry

a) increased algal growth, requires carbon uptake, initial change would be CO_2 absorption by oceans from atmosphere, reducing CO_2 mixing ratio. The long term effects depend on the ultimate fate of the additional algae.

b) stronger (deeper) penetration of UV radiation to lower in the atmosphere, could cause destruction of upper tropospheric greenhouse gases (CFCs, N_2O etc.) reducing their residence times, and lowering their concentrations.

c) If the tropospheric concentration of ozone increased, since it is a greenhouse gas and absorbs strongly in the IR region between 9 and 10 µm, it will contribute directly to an increase in warming.

d) Under the conditions given it is likely that less methane will be produced - along with a lower crop yield. The course sandy soil will likely be better aerated than the less easily drained clay soils. However, water use efficiency is much reduced.

11. One ‘climate engineering’ proposal for reducing the possibilities of global warming is to inject a sulphate aerosol into the stratosphere. Discuss the climatic and other atmospheric implications of this possible human intervention.

Solution

The injection of sulphate aerosols would cause back-scattering of incoming short-wave solar radiation in the stratosphere. This would lead to a cooling effect. A natural event of this type occurs when a volcano erupts in a sufficiently violent manner and injects volcanic debris, including sulfate particles, into the stratosphere. The effect of a volcanic eruption on the Earth's climate is then a prolonged cooling of the troposphere. The stratosphere is a very stable (temperature-inverted) region that does not mix readily within itself, or with the troposphere. Particles are not efficiently removed and have a long residence time, thus allowing for a longer period for cooling, compared with particles in the troposphere. Importantly, the simple cooling effect described here is only part of a complex set of processes, with the possibility of many other less predictable consequences. For example, we have seen that sulphate forms a nucleation centre for aqueous aerosols, and similar types of reactions could occur in the stratosphere. We have also seen that water-based aerosols play a role in stratospheric ozone chemistry.

12. Tetrafluoromethane and hexafluoroethane produced during aluminium production are potent greenhouse gases, both having GWP values of approximately 10 000. Carbon dioxide is also released from the stoichiometric reduction of alumina by carbon. Use the figures given in the text to estimate the relative global warming impact over a 100 y period from these two sources.

Solution

CF_4 and CF_3CF_3 (GWP = 10 000 for both)

Alumina (Al_2O_3) : $2Al_2O_3\ (s) + 3C\ (s) \rightarrow 4Al\ (s) + 3CO_2\ (g)$

Use Equation 8.11 (Section 8.3)

$$\mathrm{GWP} = \frac{{}_0\int^t a_i\,(t)}{\int^t a\,(t)}$$

where;

$a_i(t)$ is the instantaneous radiative forcing due to a unit increase in the concentration of the gas i. The ratio of a_i/a_0 is equivalent to the RIRF value.
$c_i(t)$ is the fraction of gas i remaining at time t
0 to t represents the time span over which integration is carried out

Figure 8.14 shows the relative share to global emissions of greenhouse gases of anthropogenic origin. Tetrafluoromethane (CF_4) and hexafluoroethane (CF_3CF_3) are not included in this diagram.

	Relative share	GWP		Concentration	
CO_2	76%	1		402	ppmv
CH_4	16%	25		1.834	ppmv
F gases	2%	7825	(average of CFC-11 & -12)	0.000791	ppmv
N_2O	6 %	298		0.328	ppmv
CF_4	trace	10 000		94	pptv (Table 8.3)
CF_3CF_3	trace	10 000		trace	

The carbon-fluorine bond is particularly strong, and so these fluorocarbon compounds would be highly stable in the troposphere. One would expect that they would exhibit similar ability to absorb IR radiation in the window region, as do chlorofluorocarbons. These combined factors would allow for you to predict that they would be ‘excellent’ and persistent greenhouse gases, with increasing concentrations over time.

13. To heat a modest-sized home during the winter in northern Europe may require approximately 2200 m^3 of natural gas per year. Calculate the amount of carbon dioxide released from the furnace over this period.

Solution

Natural gas is a naturally occurring mixture of gaseous hydrocarbons, whose approximate composition is 85 % methane, 10 % ethane, 3 % propane, and 2% butane. It is possible that natural gas may contain small amounts of other higher alkanes, but we will ignore these for this calculation.

The total number of moles of gas is determined by PV= nRT, assuming P° and 288 K

$$n = 93100 \text{ moles}$$

moles of CH_4 (x 0.85)	=	79135	which produces		79135 moles CO_2
moles of CH_3CH_3 (x .10)	=	9310	“ “	(x 2)	18620 moles CO_2
moles of $CH_3CH_2CH_3$ (x 0.03)	=	2793	“ “	(x 3)	8379 moles CO_2
moles of $CH_3CH_2CH_2CH_3$ (x 0.02)	=	1862	“ “	(x 3)	7448 moles CO_2

The total number of moles of CO_2 produced is approximately 114 000 moles or about 5.0 t of carbon dioxide per year, assuming 100% combustion.

14. Estimate the amount (kg) of carbon dioxide emissions associated with the use of 2000 kWh of electricity per month over a one year period. Consider two cases: (a) electricity produced through burning coal and (b) electricity produced through natural gas combustion.

Solution

a) 2000 kWh (per month) of electricity is equivalent to 7.2 x 10^9 J (See Table 8.6 for conversion factors). The amount of coal needed for this much energy is

$$7.2 \text{ x } 10^{9} \text{ J} / 2.5 \text{ x } 10^{10} \text{ J t}^{-1} = 0.288 \text{ t (per month)}$$

(Note: 2.5 x10^{10} J t^{-1} is an average of all coal values in Table 8.6, alternatively you could choose just one)

Using Equation 8.12, for coal

$$C + O_2 \rightarrow CO_2 \quad (\Delta H = -393.5 \text{ kJ mol}^{-1})$$

$$7.2 \text{ x } 10^{9} \text{ J} / 393\,500 \text{ J mol}^{-1} = 18297 \text{ mol (of C or } CO_2)$$

$$18\,297 \text{ mol x } 44.01 \text{ g mol}^{-1} / 1000 \text{ g kg}^{-1} = 805 \text{ kg } CO_2 \text{ per month}$$

$$= 9660 \text{ kg } CO_2 \text{ per year.}$$

b) 2000 kWh (per month) of electricity is equivalent to 7.2 x 10^9 J (See Table 8.6 for conversion factors). The amount of natural gas needed for this much energy is

$$7.2 \text{ x } 10^{9} \text{ J} / 3.7 \text{ x } 10^{7} \text{ J m}^{-3} = 195 \text{ m}^{3} \text{ (per month)}$$

Using Equation 8.13 for natural gas (assuming 100% methane)

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (\Delta H = -890.3 \text{ kJ mol}^{-1})$$

$$7.2 \text{ x } 10^{9} \text{ J} / 890\,300 \text{ J mol}^{-1} = 8087 \text{ mol (of } CH_4 \text{ and of } CO_2)$$

$$8087 \text{ mol x } 44.01 \text{ g mol}^{-1} / 1000 \text{ g kg}^{-1} = 356 \text{ kg } CO_2 \text{ per month}$$

$$= 4272 \text{ kg } CO_2 \text{ per year.}$$

The Amount of CO_2 produced burning coal is 9660 kg y^{-1}, compared to only 4272 kg y^{-1} of CO_2 when using methane to produce 24 000 kWh of electricity.

15. Estimate the area of solar collector surface required to produce all the world's electricity that is currently produced by nuclear power – The British Petroleum *Statistical review of world energy* indicates that the 2007 figure for nuclear power consumption was 622 million tonnes of oil equivalent (TOE).

Solution

Assume the value of 6.22×10^8 t (TOE) is on an annual basis. Use the value provided for petroleum (See Table 8.6 for conversion factor).

$6.22 \times 10^8 \text{ t y}^{-1} \times 3.9 \times 10^{10} \text{ J t}^{-1} = 2.43 \times 10^{19} \text{ J y}^{-1}$

Convert to kWh (1 kWh = 3.6×10^6 J)

$2.43 \times 10^{19} \text{ J y}^{-1} \div 3.6 \times 10^6 \text{ J/kWh} = 6.75 \times 10^{12} \text{ kWh y}^{-1}$

A typical value for solar panel energy production is 5 kWh/m^2/day = 1825 kWh/m^2/y

$6.75 \times 10^{12} \text{ kWh y}^{-1} / 1825 \text{ kWh/m}^2\text{/y} = 3.7 \times 10^9 \text{ m}^2 = 3.7 \times 10^3 \text{ km}^2$

The area needed would equal 3700 square kilometres.

16. In a life cycle assessment of various power generation systems (*Live-cycle analysis of power generation systems*, Central Research Institute of Electric Power Industry, March 1995), the following greenhouse gas emissions equivalents have been suggested. All values are in g of CO_2 kWh^{-1}

Hydro, 2 to 48; coal (modern plant), 790 to 1182; nuclear, 2 to 59; natural gas (co-generation), 389 to 511; biomass (forestry waste combustion), 15 to 101; wind, 7 to 124; solar (photovoltaic), 13 to 731.

(a) Recalculate the values for coal in terms of kg CO_2 GJ^{-1}, and compare these with the value (112 kg GJ^{-1}) given in the text.

(b) In general terms, comment on possible sources of greenhouse gas emissions associated with each of the generation options.

Solution

a) Using 1 kWh = 3.6×10^6 J (Table 8.6) there are 2.78×10^{-7} kWh J^{-1}

For coal: $0.790 \text{ kg } CO_2 \text{ kWh}^{-1} \times 2.78 \times 10^{-7} \text{ kWh J}^{-1} \times 10^9 \text{ J GJ}^{-1} = 219 \text{ kg } CO_2 \text{ GJ}^{-1}$

$1.182 \text{ kg } CO_2 \text{ kWh}^{-1} \times 2.78 \times 10^{-7} \text{ kWh J}^{-1} \times 10^9 \text{ J GJ}^{-1} = 329 \text{ kg } CO_2 \text{ GJ}^{-1}$

The range of 219 – 329 kg CO_2 GJ^{-1} is on the order of 2-3 times higher than the value presented in the text.

b) Generation options: possible greenhouse gas emissions (CO_2, N_2O, CH_4)

i) Hydro: low CO_2; possible source of CH_4
ii) Coal: high CO_2
iii) Nuclear (co-generation): low CO_2
iv) Natural gas: moderate CO_2
v) Biomass: low to moderate CO_2; possible CH_4 source; possible N_2O

vi) Wind: low CO_2
vii) Solar (photovoltaic): low to moderate CO_2

17. Use the information in Example 8.1 and following to predict the theoretical mass ($g\ m^{-2}\ d^{-1}$) of carbohydrate that could be produced by photosynthesis in one square metre in one day. Compare this with the actual maximum values provided to show the overall efficiency of conversion.

Solution

See Example 8.1 and surrounding text for additional data. Carbohydrate = $\{CH_2O\}$, (~ 30 $g\ mol^{-1}$)

The amount of energy absorbed at the Earth's surface is 160 GJ $ha^{-1}\ d^{-1}$, and there are 10 000 square meters per ha, which means each square meter absorbs 16 000 kJ d^{-1}. The amount of energy needed to produce 1 mole of fixed C ($\{CH_2O\}$) is 1660kJ.

16 000 kJ $m^{-2}\ d^{-1}$ / 1660 kJ mol^{-1} = 9.64 mol $m^{-2}\ d^{-1}$ of $\{CH_2O\}$

9.64 mol $m^{-2}\ d^{-1}$ x 30 g mol^{-1} = 289 g $m^{-2}\ d^{-1}$ of $\{CH_2O\}$ (theoretical mass)

Actual mass of C4 plants is 22 g $m^{-2}\ d^{-1}$, which means 22 / 289 x 100% = 7.6% efficient

Actual mass of C3 plants is 13 g $m^{-2}\ d^{-1}$, which means 13 / 289 x 100% = 4.5% efficient

18. How much CO_2 is released from the combustion of ethanol sufficient to generate 100 GJ of energy?

Solution

$$CH_3CH_2OH + 3.5O_2 \rightarrow 2CO_2 + 3H_2O \quad (\Delta H = -1367\ kJ\ mol^{-1})$$

100 GJ = 1×10^{11} J

$$1 \times 10^{11}\ J / 1\ 367\ 000\ J\ mol^{-1} = 73153 \text{ moles of ethanol } (x\ 2 = 146\ 306 \text{ moles } CO_2)$$

$$146\ 305.78\ mol \times 44.01\ g\ mol^{-1} = 6\ 438\ 917.3\ g = 6.44\ t \text{ of } CO_2$$

The amount of CO_2 released from the combustion of ethanol sufficient to generate 100GJ of energy is about 6 t.

19. Although it took many years to be established, the Montreal Protocol regarding CFCs, was an international environmental agreement that has proved to achieve some measure of success. What additional challenges complicate negotiations surrounding an international agreement on climate change issues?

For classroom discussion, no solution provided. There are many important issues including culture, resources, location, economics, wealth, etc., that can be addressed during a classroom discussion.

20. Assuming the daily water (20 000 m^3) used for extraction of the oil sands was heated from 15°C to 100°C, calculate the amount of energy needed for this process. How much CO_2 is produced, assuming the energy was obtained by burning natural gas.

Solution

Use a general thermodynamic equation for calculating heat (q), which is essentially the energy required.

$$q = mc\Delta T$$

Assume 1.00 L of water and assume the density of water is 1.00 g mL^{-1}.

m = mass of water (1000 g)

c = specific heat capacity of water 4.18 J K^{-1} g^{-1}

ΔT = change in temperature (final – initial) in K

Using 1.00 L water, the energy needed to raise the temperature from 15°C to 100°C (which is equal to 85 K), is calculated using

$$q = 1000 \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \times 85 \text{ K} = 355300 \text{ J} = 355.3 \text{ kJ}$$

Convert from cubic metres to litres: 20 000 m^3 = 20 000 000 L

The amount of energy needed to raise 20 000 000 L of water from 15°C to 100°C is

$$20\,000\,000 \text{ L} \times 355.3 \text{ kJ L}^{-1} = 7\,106\,000\,000 \text{ kJ}$$

Assume the energy required comes from natural gas.

1 m^3 of natural gas produces 3.7×10^7 J of energy (Table 8.6).

7 106 000 000 000 J / 3.7×10^7 J m^{-3} = 192 054 m^3 of natural gas.

Referring to Equation 8.13, $CH_4 + 2O_2 \rightarrow CO_2 + 2\,H_2O \quad \Delta H_{comb} = -890.3$ kJ/mol

The reactions shows that one mole of CO_2 is produced for each 890.3 kJ of energy produced from the natural gas.

$$7\,106\,000\,000 \text{ kJ} / 890.3 \text{ kJ/mol } CO_2 = 7\,981\,579 \text{ mol of } CO_2$$

Mass of CO_2 produced is:

$$\begin{aligned} 7\,981\,579 \text{ mol} \times 44.009 \text{ g mol}^{-1} &= 3.51\times10^8 \text{ g } CO_2 \\ &= 3.51\times10^5 \text{ kg } CO_2 \\ &= 0.351 \text{ Gg } CO_2 \quad (\text{See Appendix C.2, 1G} = 10^9) \end{aligned}$$