Problem Set #1

① a good approximation can be found by integrating a column to space

$$n = n_{surface} \iiint \exp\left(\frac{-(r-r_0)}{H}\right) r^2\, dr \sin\theta\, d\theta\, d\phi$$

$r - r_0 \equiv z \qquad n_{surface} = 2.5 \times 10^{19}\ cm^{-3} = 2.5 \times 10^{26}\ m^{-3}$

because $r_0 \gg z = 0 \sim 100$ km, this simplifies to

$$N_T = 4\pi R_{earth}^2\, n_s \int_{14}^{\infty} \exp(-z/H)\, dz$$

$R_{earth} \sim 6.4 \times 10^6$ m

$H \sim 7.2 \times 10^3$ m $= \frac{R^*T}{Mg} \sim \frac{8.14 \cdot 250}{.029 \cdot 9.8} \sim 7.2$ km

$$N_T = 4\pi R_{earth}^2\, n_s H \left(-\exp(-\infty) + \exp\left(\frac{-14}{7.2}\right)\right)$$

a.) $N_T \sim 1.3 \times 10^{44}$ molecules.

b.) Assume CO_2 is well mixed. $M_{CO_2} = 0.044$ kg/mole

$X_{CO_2} = 370 \times 10^{-6}$

$$M_{CO_2} = \left(N_T / 6.02 \times 10^{23}\right) \cdot 0.012 \cdot 370 \times 10^{-6}$$

$$M_{CO_2} = 9.6 \times 10^{14}\ kg = 0.96\ GTons$$

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(2.) with eddy diffusion, all molecules have the same scale height $H^{air} \equiv R^*T/M_{air}g$

$$n_j^{eddy} = n_j^{eddy}(z=0)\exp(-z/H^{air})$$

assume T = 250 K. ↑ proportional to partial pressure

The total column abundance is conserved. It equals

$$\int n_j^{eddy} dz = n_j(z=0)\int_0^\infty \exp(-z/H)dz = n_j(z=0)H^{eddy}$$

a.) After eddy mixing ceases, molecular diffusion redistributes the molecules by mass. Now each molecule has its own scale height: $H_j = \frac{R^*T}{M_j g}$ $R^* = 8.314 \frac{J}{mol K}$ $g = 9.8\ ms^{-2}$

1. so, $n_j^{mol} = n_j^{mol}(z=0)\exp(-z/H_j)$

but molecules are conserved: $n_j^{eddy}(z=0)H^{air} = n_j^{mol}(z=0)H_j$

so that $n_j^{mol} = n_j^{eddy}(z=0)\frac{H^{air}}{H_j}\exp(-z/H_j)$

(b.) The ratio at any height is:

(c.) $$\frac{n_j^{mol}}{n_j^{eddy}} = \frac{H^{air}}{H_j}\exp\left(-z\left(\frac{1}{H_j} - \frac{1}{H^{eddy}}\right)\right)$$

gas	M_j (kg/mole)	$H_j = \frac{R^*(250)}{M_j g}$ (km)	$\frac{n_j^{mol}}{n_j^{eddy}}$ z=0	z=30 km
air	0.029	7.31		
Ar	0.040	5.30	1.38	0.29
CO_2	0.044	4.82	1.52	0.18
N_2	0.028	7.57	0.97	1.12
O_2	0.032	6.63	1.10	0.72

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② d.) To do this problem properly requires integration over height. However, we know that the molecular diffusion coefficient, D, is proportional to 1/pressure. So, diffusion should be slowest near the surface. We can get an estimate by considering moving the molecules the difference in the eddy-driven scale height and the molecular diffusion driven scale height

$D \sim \frac{1}{(m)^{1/2}}$. This mass dependence is not significant

use $D = 2\times10^{-5}\ m^2\ s^{-1} = 2\times10^{-11}$

$$\tau \sim \frac{\langle H_j - H_{air} \rangle^2}{2D}.$$ The slowest should be CO_2

$$\tau = \frac{\langle 7.3 - 4.8 \rangle^2}{2(2\times10^{-11})} = 1.6\times10^{11} \text{ seconds} \sim 5000 \text{ years}$$

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(3) units = kcal/mol

a. $O + N_2O \rightarrow 2NO$

$\Delta H = 2(21.6) - (59.6 + 19.6) = -36$

exothermic

b. $O(^1D) + N_2O \rightarrow 2NO$

$\Delta H = 2(21.6) - (105 + 19.6) = -81.4$

exothermic

c. $O_3 + H_2O \rightarrow 2OH + O_2$

$\Delta H = 2(9.3) + 0 - (34.1 + (-57.8)) = 42.3$

endothermic

d. $Cl + CH_4 \rightarrow H + CH_3Cl$

$\Delta H: 52.1 + (-19.6) - (28.9 - 17.9) = 21.5$

endothermic

e. $OH + HCl \rightarrow H_2O + Cl$

$\Delta H = -57.8 + 28.9 - (9.3 - 22.1) = -16.1$

exothermic

(4) a.) $O_2 + h\nu \rightarrow 2O$ $\quad h\nu = 2(59.6) - 0 = 119.2$

$\lambda(nm) = \frac{2.86 \times 10^4}{\Delta H (kcal/mole)} = \frac{2.86 \times 10^4}{119.2} = 240\ nm$

b.) $CCl_3F + h\nu \rightarrow CCl_2F + Cl$ $\quad h\nu = -22 + 28.9 - (-68.1) = 75$

$\lambda(nm) = 381.3\ nm$

c.) $CF_4 + h\nu \rightarrow CF_3 + F$ $\quad h\nu = -112 + 19 - (-223) = 130$

$\lambda(nm) = 220\ nm$

d.) $O_3 + h\nu \rightarrow O(^1D) + O_2$ $\quad h\nu = 104.9 + 0 - 34.1 = 70.8$

$\lambda(nm) = 404\ nm$

PS#1

(5) $K.E. = \frac{1}{2}\rho v^2$

altitude (km)	ρ (kg/m³)	v (m/s)	K.E. (J)
0	1.2	460	1.3×10^5
50	10^{-3}	450	100
500	5×10^{-13}	1220	3.7×10^7

mean molecular speed changes little with height; density greatly decreases.

(6.)