

Problem Set #1

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



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

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

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

$$N_T = 4\pi R_{\text{earth}}^2 n_s \int_0^{\infty} \exp(-z/H) dz$$

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

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

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

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

- b) Assume CO_2 is well mixed. $M_{\text{CO}_2} = 0.044 \text{ kg/mole}$
 $X_{\text{CO}_2} = 370 \times 10^{-6}$

$$M_{\text{CO}_2} = (N_T / 6.02 \times 10^{23}) \cdot 0.044 \cdot 370 \times 10^{-6}$$

$$M_{\text{CO}_2} = 9.6 \times 10^{14} \text{ kg} = 0.96 \text{ GTons}$$

PS #1

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

assume $T = 250$ K. $n_j^{eddy} = n_j^{eddy}(z=0) \exp(-z/H_{air}^{eddy})$
 ↑ proportional to partial pressure

The total column abundance is conserved. It equals

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

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

so, $n_j^{mol} = n_j^{mol}(z=0) \exp(-z/H_{j,mol})$

but molecules are conserved: $n_j^{eddy}(z=0) H_{air}^{eddy} = n_j^{mol}(z=0) H_{j,mol}$
 so that $n_j^{mol} = n_j^{eddy}(z=0) \frac{H_{air}^{eddy}}{H_{j,mol}} \exp(-z/H_{j,mol})$

(b) The ratio at any height is:

(c) $\frac{n_j^{mol}}{n_j^{eddy}} = \frac{H_{air}^{eddy}}{H_{j,mol}} \exp(-z(\frac{1}{H_{j,mol}} - \frac{1}{H_{air}^{eddy}}))$

gas	M_j (kg/mol)	$H_{j,mol} = \frac{R^*(250)}{M_j g}$ (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

PS #1

② d.) To do this problem properly requires integration over height. However, we know that the molecular diffusion coefficient, D , is proportional to $1/\text{pressure}$. 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 $D = 2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} = 2 \times 10^{-11}$

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

$$\tau = \frac{\langle 7.3 - 4.8 \rangle^2}{2(2 \times 10^{-11})} = 1.6 \times 10^{11} \text{ seconds} \sim 5000 \text{ years}$$

PS #1

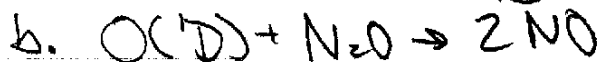
③

units = kcal/mol



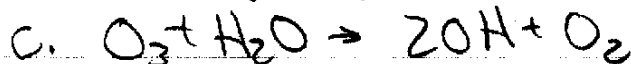
$$\Delta H = 2(21.6) - (59.6 + 19.6) = -36$$

exothermic



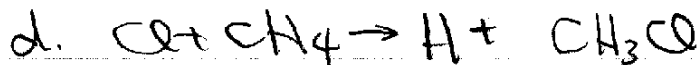
$$\Delta H = 2(21.6) - (105 + 19.6) = -81.4$$

exothermic



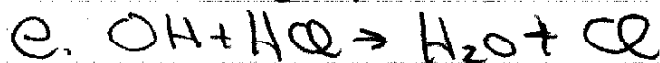
$$\Delta H = 2(9.3) + 0 - (34.1 + (-57.8)) = 42.3$$

endothermic



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

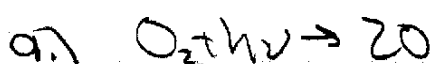
endothermic



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

exothermic

④

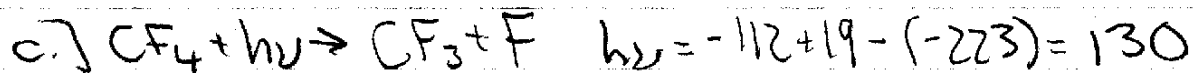


$$h\nu = 2(59.6) - 0 = 119.2$$

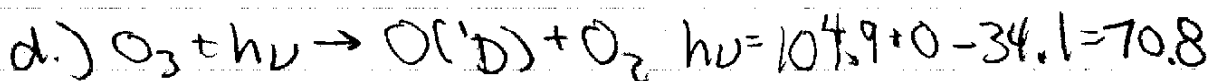
$$\lambda(\text{nm}) = \frac{2.86 \times 10^4}{\Delta H(\text{kcal/mole})} = \frac{2.86 \times 10^4}{119.2} = 240 \text{ nm}$$



$$\lambda(\text{nm}) = 381.3 \text{ nm}$$



$$\lambda(\text{nm}) = 220 \text{ nm}$$



$$\lambda(\text{nm}) = 404 \text{ nm}$$

PS#1

⑤ $K.E. = \frac{1}{2} \rho v^2$

altitude (km)	ρ (kg/m ³)	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.