



**The next two problems are related.**

Radon is a radioactive noble gas (atomic weight 0.222 kg/mole) that leaks from the ground and often gets trapped in homes.

1. What is the average translational kinetic energy of a single radon molecule at room temperature (20° C)?

a.  $1.01 \times 10^{-20}$  J

b.  $6.07 \times 10^{-21}$  J

c.  $2.76 \times 10^{-22}$  J

d.  $4.14 \times 10^{-22}$  J

e. Cannot be determined with the information given.

$$\langle KE \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT \approx 1.5 (1.38 \times 10^{-23}) (293K) = 4.14 \times 10^{-22} J$$

$$\langle v \rangle = 0$$

$$m = \frac{0.222 \text{ kg}}{6 \times 10^{23}}$$

$$v \approx v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3 \langle KE \rangle}{m}} = 181 \text{ m/s}$$

2. Even though it becomes trapped, there is only  $10^{-18}$  kg/m<sup>3</sup> of Radon gas at any one time due to its short half-life. What partial pressure does it exert in the home at room temperature?

a.  $1.1 \times 10^{-14}$  Pa

b.  $1.1 \times 10^{-16}$  Pa

c.  $2.4 \times 10^{-14}$  Pa

d.  $2.4 \times 10^{-16}$  Pa

e. Cannot be determined with the information given.

$$pV = NkT = nRT$$

$$p = \frac{n}{V} RT = \frac{10^{-18} \text{ kg}}{\text{m}^3} \cdot \frac{1 \text{ mole} (8.314)}{0.222 \text{ kg}} = 3.74 \text{ Pa}$$



3. The noble gasses He and Ar can be used to raise and lower the pitch of your voice respectively. What is the approximate ratio of the speed of sound of He to that of Ar,  $v_{\text{He}}/v_{\text{Ar}}$ ?

a.  $\sqrt{\frac{1}{10}}$

b.  $\sqrt{\frac{1}{2}}$

c. 1

d.  $\sqrt{2}$

e.  $\sqrt{10}$

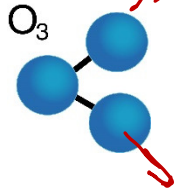
$$K E_{\text{trans}} = \frac{1}{2} m_{\text{He}} \langle v_{\text{He}}^2 \rangle = \frac{3}{2} kT = \frac{1}{2} m_{\text{Ar}} \langle v_{\text{Ar}}^2 \rangle$$

$$\frac{v_{\text{He, rms}}}{v_{\text{Ar}}} = \sqrt{\frac{m_{\text{Ar}}}{m_{\text{He}}}} = \sqrt{10}$$

$$m_{\text{Ar}} = 40 \text{ g/mol}$$

$$m_{\text{He}} = 4 \text{ g/mol}$$

The next two problems refer to the following situation:



Ozone (O<sub>3</sub>) is a non-linear molecule (as shown in figure). Assume the O<sub>3</sub> and O<sub>2</sub> gasses below are at the same temperature and neglect vibrational energy.

4. Which has more total internal energy, 2 moles of O<sub>3</sub> or 3 moles of O<sub>2</sub>?

- a. 2 moles of O<sub>3</sub>
- b. 3 moles of O<sub>2</sub>**
- c. They contain the same internal energy.

$\begin{array}{c} \text{O}_2 \\ 3R\left(\frac{5}{2}\right) \\ 7.5R \end{array}$	$\begin{array}{c} \text{O}_3 \\ 2R(3) \\ 6R \end{array}$
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5. Which has a higher translational kinetic energy?

- a. O<sub>2</sub>
- b. O<sub>3</sub>
- c. They are the same.**

$$\frac{U_{KE,trans}}{\text{molecule}} = \frac{3}{2} kT$$

$$U = \alpha N k T = \alpha n R T$$

$$\alpha_{\text{monatomic}} = \frac{3}{2} \quad \left[ \begin{array}{l} 3 \text{ trans} \\ 0 \text{ rot} \\ 0 \text{ vib} \end{array} \right]$$

$$\alpha_{\text{diatomic}} = \frac{1}{2} [3 + 2] = \frac{5}{2}$$

$$\alpha_{\text{nonlinear}} = \frac{1}{2} [3 + 3] = 3$$

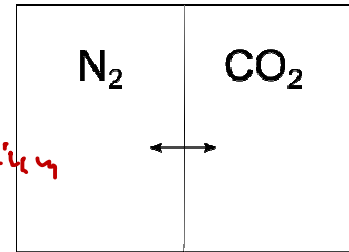
T high enough that there's lots of vibrations  
 $kT \gg hf$

$$\alpha_{\text{diatomic}} = \frac{1}{2} (3 + 2 + 2) \quad (+2 \text{ for } 5 \text{ Ho})$$

$$\alpha_{\text{O}_3} = \frac{1}{2} (3 + 3 + 4)$$

(3 moles of O<sub>2</sub> would have more U<sub>KE,trans</sub> than 2 moles of O<sub>3</sub>)

6. Two 30-m<sup>3</sup> volumes are separated by a moveable barrier. 1000 kg of N<sub>2</sub> is in the left volume and 1000 kg of CO<sub>2</sub> is in the right volume. Assuming the system is kept at a constant temperature, which way does the barrier start to move when released?



- a. left
- b. right
- c. It doesn't move.

Method 1:  $P_L = P_R$  in equilibrium

$$n_{N_2} \frac{RT}{V_L} = n_{CO_2} \frac{RT}{V_R}$$

$$\frac{V_L}{V_R} = \frac{n_{N_2}}{n_{CO_2}} = \frac{1000 \text{ kg} / (0.028 \text{ kg/mole})}{1000 \text{ kg} / (0.044 \text{ kg/mole})} = \frac{0.044}{0.028} > 1$$

Maximize total entropy

$$\sigma_{TOT} = \sigma_L + \sigma_R$$

$$\frac{d\sigma_{TOT}}{dV_L} = 0 = \frac{d\sigma_L}{dV_L} + \frac{d\sigma_R}{dV_L} = \frac{d\sigma_L}{dV_L} - \frac{d\sigma_R}{dV_R} \quad (dV_L = -dV_R)$$

$$\sigma = \ln \Omega = \ln(V \lambda^{-3N}) = N \ln V + \text{const}$$

$$\frac{N_L}{V_L} = \frac{d\sigma_L}{dV_L} = \frac{d\sigma_R}{dV_R} = \frac{N_R}{V_R}$$

$$N_L > N_R$$

$$P_L = P_R$$

$$F_L = F_R$$

$$L = \frac{1}{N}$$

$$\frac{\Delta p}{\Delta t} = \frac{m N^2 (\# \text{mol})}{L}$$

Both sides have same  $m \langle v^2 \rangle (=3kT)$

So just  $N_{N_2}$  vs  $N_{CO_2}$

7. What temperature would an ideal gas of hydrogen molecules ( $H_2$ ) need to be in order for the average speed of each molecule to slow down to 100 m/s?

- a. 0.4 K
- b. 0.8 K
- c. 4 K
- d. 8 K
- e. 40 K

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT$$

~~So~~  $T = \frac{m v^2}{3k}$

$$= \frac{0.002 \text{ kg} \cdot \text{m}^2}{3 \cdot \underbrace{N_A k}_{= R}} = \frac{0.002 \text{ kg}}{3 \cdot 8.314} \times (100 \text{ m/s})^2$$

The next two problems refer to the following situation:

Suppose that we are given one mole of a complicated solid with an internal energy per particle of  $U=3kT+\eta(kT)^2$  where  $\eta=7.4 \times 10^{20} \text{ Joules}^{-1}$ .

8. What is the heat capacity (at constant volume) when the temperature  $T=300\text{K}$ ?

- a. 24.9 J/K
- b. 50.4 J/K
- c. 75.9 J/K

$Q = U + W_{by}$   
 $dQ = dU + p dV$   
 $U = 3kT + \eta k^2 T^2$   
 $C_{\text{atom}} = 3k + 2\eta k^2 T$   
 $C_{\text{mole}} = C_{\text{atom}} (N_A)$

$C = \frac{dQ}{dT} = \frac{dU}{dT}$

9. Suppose that we heat the solid; what can we say about the *change* in internal energy in the following two scenarios: (A) starting from  $T=300\text{K}$ , the temperature of the solid increases by  $2\text{K}$  and the volume stays constant, or (B) starting from  $T=320\text{K}$ , the temperature of the solid increases by  $2\text{K}$  and the volume stays constant?

- a. The internal energy increases more in scenario A.
- b. The internal energy increases more in scenario B.
- c. The change in internal energy is non-zero and the same in both cases.
- d. The internal energy does not change in either case.
- e. Nothing can be determined from the given information.

$\Delta U(300 \rightarrow 302)$   
 $\frac{1}{T} = \frac{\partial U}{\partial T}$

$\partial U = \frac{\partial U}{\partial T} dT = \frac{C dT}{T}$

$\Delta U = \int_{T_i}^{T_f} \frac{C dT}{T} = \int (3N_A k + 2\eta k^2 N_A T) dT = 3N_A k \ln \frac{T_f}{T_i} + 2\eta k^2 N_A \times (T_f - T_i)$

$\Delta U = C(T) \Delta T$   
 Since:  $C(320) > C(300)$   
 $\Delta U(320 \rightarrow 322) > \Delta U(300 \rightarrow 302)$

The next three problems refer to the following situation:

Suppose that a thin spherical shell of Aluminum (density  $2.7 \times 10^3 \text{ kg/m}^3$ ) with inner radius  $R_i=4\text{m}$  and outer radius  $R_o=4.01\text{m}$  is immersed in an extremely cold liquid. The shell is filled with a monatomic gas, and the initial temperature of the Aluminum and the contained gas is 293 K. Assume that we can treat the liquid bath as a heat reservoir at temperature 3K.

10. If the thermal conductivity of Aluminum is  $200 \text{ W/(m}\cdot\text{K)}$ , calculate the initial heat-flow, right after the sphere is immersed in the bath.

- a.  $1.16 \times 10^9 \text{ W}$
- b.  $1.57 \times 10^9 \text{ W}$
- c.  $2.90 \text{ W}$

$$H = \frac{\Delta T}{R_{th}} \quad R_{th} = \frac{d}{kA} \rightarrow \text{Surface area}$$

$$H = J \times A$$

$$\frac{J \cdot K}{d}$$

$$= \frac{290\text{K}}{(0.01\text{m})} \frac{200\text{W}}{\text{m}\cdot\text{K}} (4\pi (4\text{m})^2)$$



11. Given that the specific heat of Aluminum is  $900 \text{ J/(kg}\cdot\text{K)}$  calculate the heat capacity of the spherical shell.

- a.  $2.45 \times 10^6 \text{ J/K}$
- b.  $4.90 \times 10^6 \text{ J/K}$
- c.  $2.43 \times 10^7 \text{ J/K}$
- d.  $4.91 \times 10^8 \text{ J/K}$
- e.  $6.56 \times 10^8 \text{ J/K}$

$$C = c \cdot m = c \rho \cdot V = c \rho (4\pi r^2 d)$$

$$= 900 (2700) 4\pi (4\text{m})^2 (0.01\text{m})$$

$$= 4.89 \times 10^6 \text{ J/K}$$

Al: 27g/mole

$$C_{mole} = nR \cdot 3$$

$$U = \frac{3}{2} N k T$$

$$C = \frac{3}{2} N k = \frac{3}{2} n R$$

$$C_{mole} = \frac{3}{2} R$$

$$\rho \epsilon = \frac{C_{mole} \frac{3}{2} R}{m_{mole} = 0.027 \text{ kg}} = \underline{924 \text{ J/kg}\cdot\text{K}}$$

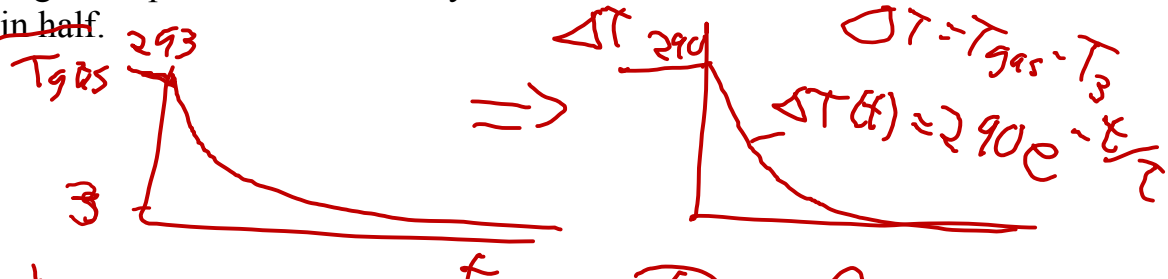
12. Consider the heat transfer process that occurs through the Aluminum between the gas inside the spherical shell and the 3K cold liquid bath outside. Which of the following statements is true?

(i) The gas inside the spherical shell will continue transferring heat to the liquid and its temperature will asymptote to absolute zero (0 K) after a long time.

(ii) The rate at which the temperature of the inside gas decreases becomes faster if a denser monatomic gas at the same temperature replaces the initial gas inside the shell.

(iii) The rate at which the inside gas changes temperature immediately after the shell is immersed doubles if the thickness of the Aluminum shell is cut in half.

- a. i only
- b. ii only
- c. iii only
- d. i and ii
- e. ii and iii



More  $\left(\frac{M}{V}\right) \Rightarrow$  more  $N$

$$C = \alpha N R$$

More  $C$

$\tau$  increase  
slower rate

$C_{gas}$   
monatomic

$$C_v = \frac{3}{2} N R$$

diatomic

$$C_v = \frac{5}{2} N R$$

Low  $T$

$\frac{3}{2} N R$   
No rotations

$$\tau = R_{th} C$$

$$R_{th} \sim d$$

$$d \rightarrow d/2$$

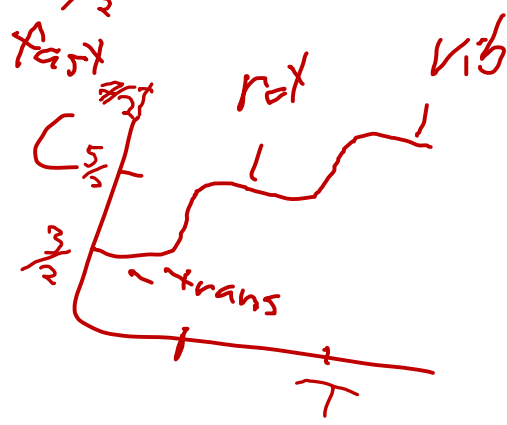
$$R_{th} \rightarrow R_{th}/2$$

$$\tau \rightarrow \tau/2$$

Twice as fast

High  $T$

$\frac{7}{2} N R$   
+ vibrations





13. Suppose that we have a particle executing random Brownian motion inside the gaseous planet Jupiter. If the particle has an average velocity of  $10^6$  m/s and an average time between collisions of 10 ms, how long, on average, will it take it to diffuse from the center of the planet to outer space (assume that the distance from the center to outer space is 69,000 km)? Calculate your answer in earth days (1 earth day = 86,400 sec).

- a. 0.53 days
- b. 2.8 days
- c. 8.3 days

Don't care what direction diffusing in

$$\langle r^2 \rangle = 6Dt$$

$$D = \frac{1}{3} v l = \frac{1}{3} v v \tau$$

Higher T  
 $l \sim \text{constant}$

$$t = \frac{r^2}{6D}$$

$$= \frac{(69 \times 10^6 \text{ m})^2}{6 \cdot \frac{1}{3} (10^6 \text{ m/s})^2 \cdot 0.01 \text{ s}}$$

$$= \frac{1}{3} \frac{v}{v^2 \tau} = \frac{l}{v \tau}$$

$$\frac{1}{2} m v^2 \sim kT$$

$$v \sim \sqrt{T} \quad D \sim \sqrt{T}$$

$$t \sim \frac{1}{\sqrt{T}}$$

$$= \frac{69^2}{2 \cdot (0.01)} = 238000 \text{ s}$$

$$= 2.76 \text{ days}$$

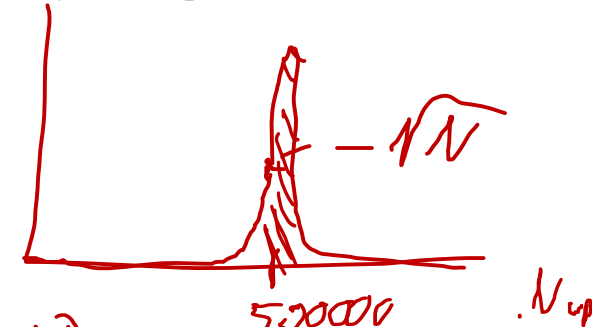
The next two problems refer to the following situation:

Consider a spin system of 1,000,000 spins where each spin is equally likely to be up (u) or down (d).

14. The probability that exactly 500,000 spins are up is

- a. greater than 50%
- b. exactly equal to 50%
- c. less than 50%

$$P = \frac{\binom{10^6}{500000}}{2^{10^6}} \approx \frac{2^{10^6}}{2^{10^6}} \approx \frac{1}{2}$$



15. Consider the following two possibilities:

- (1) All the spins are up. *uuuuu*
- (2) All odd spins are up and all even spins are down (i.e. udududu...)

Which of the following statements are true:

- a. (1) and (2) are equally likely
- b. (1) is more likely than (2)
- c. (2) is more likely than (1)

$$P = \left(\frac{1}{2}\right)^{10^6}$$

Both just single microstates

All microstates equally likely

$$\begin{aligned} & \approx \frac{2^N e^{-N^2/2N}}{2^N} \sqrt{\frac{2}{\pi N}} \\ & = \sqrt{\frac{2}{\pi 10^6}} = 8 \times 10^{-4} \\ & \text{Area} \sim 8 \times 10^{-4} \sqrt{10^6} \\ & \approx 0.8 \end{aligned}$$

$n = N_{up} - N_{down} = 0$

$N_2$	$Ar$
100K	200K

The next three problems are related.

16. Consider two boxes that are separated. Both boxes are  $1\text{-m}^3$ . The first box is filled with 1 mole of  $N_2$  at 100K and the second box is filled with 1 mole of  $Ar$  at 200K. The two boxes are placed into contact so heat can transfer between them. What is the final temperature?

- a. 137.5 K
- b. 150.0 K
- c. 162.5 K

$$Q = qnR$$

$$|Q_{Ar}| = |Q_{N_2}|$$

$$C_{Ar} \Delta T_{Ar} = C_{N_2} \Delta T_{N_2}$$

$$C_{Ar} (200 - T_f) = C_{N_2} (T_f - 100)$$

$$T_f (C_{Ar} + C_{N_2}) = C_{Ar} T_{Ar} + C_{N_2} T_{N_2}$$

$$C_{Ar} = \frac{3}{2} R$$

$$C_{N_2} = \frac{5}{2} R$$

$$= \frac{\frac{3}{2} R \cdot 200 + \frac{5}{2} R \cdot 100}{\frac{3}{2} R + \frac{5}{2} R} = \frac{3 \cdot 200 + 5 \cdot 100}{3 + 5}$$

17. Now suppose the wall between the two boxes is removed after they have equilibrated. What is the change in the total entropy before and after removing the partition?

- a. 11.5 J/K
- b. 23.1 J/K
- c. 5.76 J/K

Start at same temp

$$\Delta S = \underbrace{2N}_{nR} \ln \frac{V_f}{V_i} = R \left[ 1 \text{ mole}_{N_2} \ln \frac{V_{f,N_2}}{V_{N_2,i}} + 1 \text{ mole}_{Ar} \ln \frac{V_{f,Ar}}{V_{Ar,i}} \right]$$

$$\Delta S(T_i \Rightarrow T_f) = C_v \ln \frac{T_f}{T_i}$$

$$\Delta S_{100} = 1.95 \text{ J/K}$$

$$S_{Ar} = \frac{3}{2} R \ln \frac{137.5}{200} = -4.67 \text{ J/K}$$

$$S_{N_2} = \frac{5}{2} R \ln \frac{137.5}{100} = 6.62 \text{ J/K}$$

$$\Delta S = (R \ln 2)^2$$

18. After the system has equilibrated from the removal of the partition, what is the probability that all the gas is on the left half of the combined box?

a.  $\left(\frac{1}{2}\right)^{1.2 \times 10^{24}}$

b.  $\left(\frac{1}{4}\right)^{3.41 \times 10^{23}}$

c.  $\left(\frac{1}{300}\right)^{2.41 \times 10^{23}}$

$$P = \frac{\Omega(A)}{\Omega_{\text{TOT}}} = \frac{1}{2^N} = \frac{1}{2^{2 \cdot N_A}}$$

$$\Omega_L = (V_L n_T)^{N_A}$$

$$\Omega(A) = (V_L n_T)^{2 \cdot N_A}$$

$$\Omega_{\text{TOT}} = (2V_L n_T)^{2 \cdot N_A}$$

$$\frac{\Omega(A)}{\Omega_{\text{TOT}}} = \frac{1}{2^{2 \cdot N_A}}$$

The next two questions are related.

On earth at sea level the partial pressure of  $N_2$  is 0.78 atm, at 270 K, but it falls off at higher altitudes. Assume that we can model this using the Boltzmann distribution for a gas in thermal equilibrium.

19. How will the ratio of the partial pressure of  $N_2$  at 1.6 km to the partial pressure of  $N_2$  at sea level change, as the temperature drops to 250 K?

- a.  $\frac{p(1.6 \text{ km}, 250 \text{ K})/p(0 \text{ km}, 250 \text{ K})}{p(1.6 \text{ km}, 270 \text{ K})/p(0 \text{ km}, 270 \text{ K})} = 0.98$
- b.  $\frac{p(1.6 \text{ km}, 250 \text{ K})/p(0 \text{ km}, 250 \text{ K})}{p(1.6 \text{ km}, 270 \text{ K})/p(0 \text{ km}, 270 \text{ K})} = 1$
- c.  $\frac{p(1.6 \text{ km}, 250 \text{ K})/p(0 \text{ km}, 250 \text{ K})}{p(1.6 \text{ km}, 270 \text{ K})/p(0 \text{ km}, 270 \text{ K})} = 1.01$
- d.  $\frac{p(1.6 \text{ km}, 250 \text{ K})/p(0 \text{ km}, 250 \text{ K})}{p(1.6 \text{ km}, 270 \text{ K})/p(0 \text{ km}, 270 \text{ K})} = 1.04$
- e.  $\frac{p(1.6 \text{ km}, 250 \text{ K})/p(0 \text{ km}, 250 \text{ K})}{p(1.6 \text{ km}, 270 \text{ K})/p(0 \text{ km}, 270 \text{ K})} = 1.06$

density

$$\frac{p(h)}{p(0)} \propto \frac{n(h)}{n(0)} \propto \frac{\text{prob}(h)}{\text{prob}(0)} = \frac{e^{-E(h)/kT}}{e^{-E(0)/kT}}$$

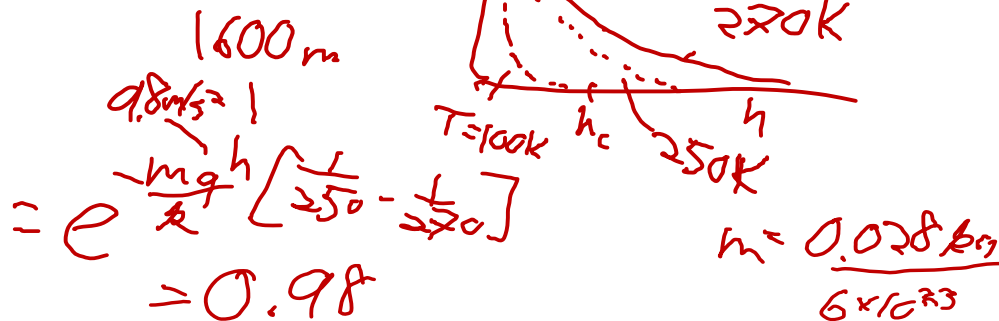
$$= e^{-mgh/kT}$$

$$= e^{-h/h_c}$$

$E(h) = mgh$   
 $h_c = \frac{kT}{mg}$

$$\frac{p(1.6, 250)}{p(0, 250)} = \frac{e^{-mgh/k \cdot 250}}{e^{-mgh/k \cdot 270}}$$

$$\frac{p(1.6, 270)}{p(0, 270)}$$



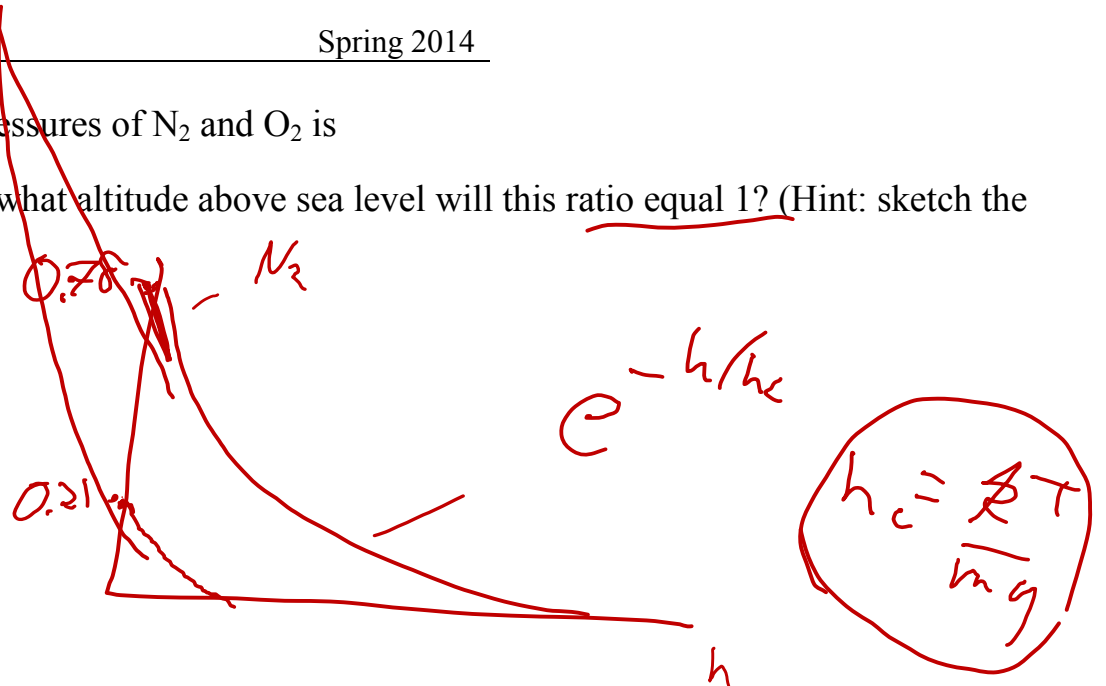
$$= e^{-\frac{mgh}{k} \left[ \frac{1}{250} - \frac{1}{270} \right]}$$

$$= 0.98$$

20. At sea level ( $h = 0$ ) the ratio of partial pressures of  $N_2$  and  $O_2$  is

$p(N_2, h=0)/p(O_2, h=0) = 0.78/0.21 = 3.7$ . At what altitude above sea level will this ratio equal 1? (Hint: sketch the pressure curves as a function of altitude.)

- a. 9.6 km
- b. 75 km
- c. There is no altitude where this occurs.



$m_{N_2} = 28 \text{ g/mol}$   
 $m_{O_2} = 32 \text{ g/mol}$

$h_{c, O_2} < h_{c, N_2}$

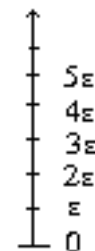
$$\frac{p_{N_2}(h)}{p_{O_2}(h)} = \frac{p_{N_2}(0) e^{-m_{N_2}gh/RT}}{p_{O_2}(0) e^{-m_{O_2}gh/RT}} = 1 = \frac{0.78}{0.21} e^{-(m_{N_2}-m_{O_2})gh/RT}$$

$$\frac{(m_{N_2}-m_{O_2})gh}{RT} = -\ln \frac{0.21}{0.78}$$

$$h = \frac{-\ln(0.21/0.78) RT}{m_{N_2}-m_{O_2}}$$

The next four problems are related.

A vibrational mode of a CO<sub>2</sub> molecule can be modeled as a harmonic oscillator.



21. Assuming the frequency of the oscillation is  $7 \times 10^{13}$  Hz (corresponding to energy levels separated by  $\epsilon = 4.6 \times 10^{-20}$  Joules, as illustrated here), what is the highest the temperature can be and still have the probability to be in the vibrational ground state ( $E = 0$ ) greater than 99%?

- a. 68 K
- b. 245 K
- c. 560 K
- d. 720 K
- e. Cannot be determined from the information given.

①

$$\epsilon = hf$$

Almost all in ground state:  $kT \ll \epsilon$

$$P(0) = \frac{e^{-E_0/kT}}{\sum_{n=0}^{\infty} e^{-E_n/kT}} = \frac{1}{1 + e^{-\epsilon/kT} + e^{-2\epsilon/kT} + \dots}$$

$$0.99 + 0.99 e^{-\epsilon/kT} = 1$$

$$e^{-\epsilon/kT} = \frac{1 - 0.99}{0.99}$$

$$\frac{\epsilon}{kT} = -\ln \frac{0.01}{0.99}$$

$$\approx \frac{1}{1 + e^{-\epsilon/kT}} \approx 0.99$$

$$T = \frac{-\epsilon}{k \ln(0.01/0.99)} = 725 \text{ K}$$

②

Formula

$$P_n = (1 - e^{-\epsilon/kT}) e^{-n \epsilon/kT}$$

$$0.99 = (1 - e^{-\epsilon/kT})$$

$$e^{-\epsilon/kT} = 1 - 0.99 = 0.01$$

$$\frac{\epsilon}{kT} = -\ln(0.01)$$

$$T = \frac{-\epsilon}{k \ln 0.01}$$

22. Compare the ratio of the probability of having exactly one quantum of energy to zero quantum of energy (i.e.,  $P(E = \epsilon)/P(E=0)$ ) vs. the ratio of the probability of having exactly two quantum of energy to one quantum of energy (i.e.,  $P(E = 2\epsilon)/P(E=\epsilon)$ ).

- a.  $P(E=\epsilon)/P(E=0) = P(E=2\epsilon)/P(E=\epsilon)$
- b.  $P(E=\epsilon)/P(E=0) > P(E=2\epsilon)/P(E=\epsilon)$
- c. Whether  $P(E=\epsilon)/P(E=0)$  is greater or less than  $P(E=2\epsilon)/P(E=\epsilon)$  depends on the temperature.

$$\frac{P(\epsilon)}{P(0)} = \frac{e^{-\epsilon/kT} / Z}{e^{0/kT} / Z} = e^{-\epsilon/kT}$$

$$\frac{P(2\epsilon)}{P(\epsilon)} = \frac{e^{-2\epsilon/kT} / Z}{e^{-\epsilon/kT} / Z} = e^{-\epsilon/kT}$$

23. What is the ratio of the heat capacity (from the vibration) of one of these molecules at low temperature ( $T \rightarrow 0$ ) to that at high temperature ( $T \rightarrow \infty$ )?

- a.  $C(T \rightarrow 0)/C(T \rightarrow \infty) = 0$
- b.  $C(T \rightarrow 0)/C(T \rightarrow \infty) = 1$
- c.  $C(T \rightarrow 0)/C(T \rightarrow \infty) = \infty$

formula

$$\langle E \rangle = \frac{\epsilon}{e^{\epsilon/kT} - 1}$$

At low T  $C(T \rightarrow 0) \rightarrow 0$   
 (nothing excited  $\rightarrow$  everything in ground state)

$C(T \rightarrow \infty) \stackrel{kT \gg \epsilon}{=} \frac{\epsilon}{kT}$   
 Equipartition  
 $C = Nk$  for SHO  
 $C = \frac{d\langle E \rangle}{dT} = k$

$$= \frac{\epsilon}{1 + \frac{\epsilon}{kT}} = kT$$



24. Suppose that there were *two* vibrational states with  $E = \epsilon$  and one with  $E = 0$  (i.e., the first excited level is degenerate). How would the probability  $P(E=0)$  to be in the ground state change (compared to the case of a non-degenerate first-excited level, and assuming  $T > 0$ )?

- a.  $P(E=0)$  would be smaller than if the first excited level had only one state.  
 b.  $P(E=0)$  would be the same as if the first excited level had only one state.  
 c.  $P(E=0)$  would be greater than if the first excited level had only one state.

More ways not to be in ground state.  
 $P(g)$  decrease

$$P(g) = \frac{e^0}{e^0 + 2e^{-\epsilon/kT} + e^{-2\epsilon/kT} + \dots} < \frac{1}{1 + e^{-\epsilon/kT} + \dots}$$