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① RG Chapter 13, problem 5

The Maxwell speed distribution is given by [RG eq (13.17) on p 312]

$$\tilde{f}(v)dv = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/2kT} 4\pi v^2 dv$$

The kinetic energy is given by

$$E = \frac{1}{2}mv^2$$

If the probability distribution for kinetic energy is given by $P(E)$, then

$$P(E)dE = \tilde{f}(v)dv$$

Since the number of molecules with speed between v and $v+dv$ is the same as the number of molecules with kinetic energy between E and $E+dE$, assuming that $E = \frac{1}{2}mv^2$.

Thus,
$$P(E) = \tilde{f}(v) \frac{dv}{dE}$$

When on the right hand side of this equation, we put $v = \sqrt{\frac{2E}{m}}$.

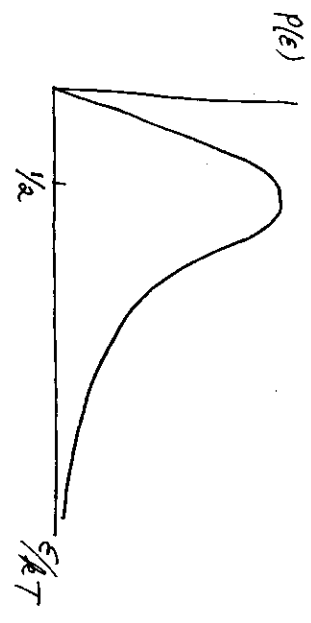
Noting that
$$\frac{dv}{dE} = \sqrt{\frac{2}{m}} \frac{1}{2} E^{-1/2}$$
,

$$P(E) = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-E/kT} \frac{4\pi}{\sqrt{m}} \left(\frac{2E}{m} \right)^{3/2} \sqrt{\frac{2}{m}} \frac{1}{2} E^{-1/2}$$

Simplifying this result, we end up with:

$$P(E) = \frac{2}{\sqrt{\pi}} \frac{1}{(kT)^{3/2}} e^{-E/kT} E^{1/2}$$

A graph of $P(E)$ looks like:



The mean value of E is given by

$$\langle E \rangle = \int_0^{\infty} E P(E) dE = \frac{2}{\sqrt{\pi}} \frac{1}{(kT)^{3/2}} \int_0^{\infty} E^{3/2} e^{-E/kT} dE$$

Substituting $x = \frac{E}{kT}$,

$$\langle E \rangle = \frac{2}{\sqrt{\pi}} kT \int_0^{\infty} x^{3/2} e^{-x} dx$$

$$= \frac{2}{\sqrt{\pi}} kT \Gamma\left(\frac{5}{2}\right)$$

Using the property of the Γ -function that $\Gamma(z+1) = z\Gamma(z)$, and recalling that $\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$,

$$\Gamma\left(\frac{5}{2}\right) = \frac{3}{2} \cdot \frac{1}{2} \sqrt{\pi}$$

Thus,

$$\langle E \rangle = \frac{3}{2} kT$$

②

3

To find the most probable value of ϵ , set $\frac{dP}{d\epsilon} = 0$ to find the maximum of the curve.

$$\frac{dP}{d\epsilon} = \frac{2}{\sqrt{\pi}} \frac{1}{(kT)^{3/2}} \left[-\frac{1}{kT} e^{-\epsilon/kT} \epsilon^{1/2} + \frac{1}{2} e^{-\epsilon/kT} \epsilon^{-1/2} \right] = 0$$

Thus,
$$\frac{\epsilon^{1/2}}{kT} = \frac{1}{2} \epsilon^{-1/2}$$

or
$$\boxed{\epsilon = \frac{1}{2} kT}$$

(mp = most probable)

Contrast this with [see RB eq. (13.18) on p. 513]

$$\frac{1}{2} m v_{mp}^2 = \frac{1}{2} m \left(\frac{2kT}{m} \right) = kT$$

These results differ, because the relation between ϵ and v is non-linear. For example,

$$\langle \epsilon \rangle \neq \frac{1}{2} m \langle v \rangle^2$$

since $\langle v \rangle = \sqrt{\frac{2kT}{\pi m}}$ [RB eq. (13.19) on p. 513].

We would not expect $\langle v \rangle^2 = \langle v^2 \rangle$ since the variance is

$$\sigma_v^2 = \langle v^2 \rangle - \langle v \rangle^2 \neq 0.$$

Similarly, the most probable value of v^2 is not the square of the most probable value of v .

4

2 RB Chapter 10, problem 4

(a) Start with [RB eqs (10.15) and (10.16) on p. 255]

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N}, \quad P = - \left(\frac{\partial F}{\partial V} \right)_{T,N}$$

Then,

$$\left(\frac{\partial S}{\partial V} \right)_{T,N} = - \left[\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T} \right)_{T,N} \right]$$

$$\left(\frac{\partial P}{\partial T} \right)_{V,N} = - \left[\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V} \right)_{T,N} \right]$$

Using

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V}$$

we conclude that

$$\boxed{\left(\frac{\partial S}{\partial V} \right)_{T,N} = \left(\frac{\partial P}{\partial T} \right)_{V,N}}$$

Using the ideal gas law, $P = \frac{NkT}{V}$. Thus, $\left(\frac{\partial P}{\partial T} \right)_{V,N} = \frac{Nk}{V}$

and thus,

$$\left(\frac{\partial S}{\partial V} \right)_{T,N} = \frac{Nk}{V}$$

⑤

Integrating this equation,

$$S = NR \ln V + f(T, N)$$

where $f(T, N)$ is an arbitrary function of T, N . This is the integration "constant" resulting from integrating $\left(\frac{\partial S}{\partial V}\right)_{T, N} = \frac{NR}{V}$.

This indeed reproduces the correct volume dependence of S for an ideal gas (see, eg. RB eg. (5.48) or p. 107).

(b) Using the results for S and P used in part (a), and

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T, V}$$

we obtain:

$$\left(\frac{\partial \mu}{\partial T}\right)_{N, T} = \left[\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial N}\right)_{T, V} \right]_{N, T}$$

$$\left(\frac{\partial \mu}{\partial N}\right)_{T, V} = - \left[\frac{\partial}{\partial N} \left(\frac{\partial F}{\partial T}\right)_{T, V} \right]_{T, V}$$

Using

$$\frac{\partial^2 F}{\partial T \partial N} = \frac{\partial^2 F}{\partial N \partial T}$$

it follows that

$$\boxed{\left(\frac{\partial \mu}{\partial V}\right)_{N, T} = - \left(\frac{\partial P}{\partial N}\right)_{V, T}}$$

⑥

For an ideal gas,

$$\left(\frac{\partial P}{\partial N}\right)_{T, V} = \frac{kT}{V}$$

Hence,

$$\left(\frac{\partial \mu}{\partial V}\right)_{N, T} = - \frac{kT}{V}$$

Integrating this equation yields:

$$\mu = -kT \ln V + g(T, N)$$

where $g(T, N)$ is an arbitrary function of T and N . This indeed reproduces the volume dependence of the chemical potential of an ideal gas (see eg. (7.20) or p. 157 of RB).

③ RB Chapter 11, problem 7

(a) Using RB eqs. (11.20) and (11.21) with $b_{H_2} = -1$ and $b_H = 2$,

$$\frac{[H]^2}{[H_2]} = K(T)$$

where $[H]$ is the concentration of H, $[H_2]$ is the concentration of H_2 and

$$K(T) = \frac{[\lambda_H^{-3} Z_{H(int)}]^2}{\lambda_{H_2}^{-3} Z_{H_2(int)}}$$

Using RB eq. (11.36),

$$Z_{H(int)} = 2 \times 2 \times e^{-\epsilon_{gs,H}/kT}$$

where the factors 2x2 represent the nuclear and electron spin degeneracy factors and ϵ_{gs} is the ground state energy of hydrogen.

Since the energy scale is arbitrary (only energy differences matter), we are free to choose the zero of the energy scale that corresponds to separated hydrogen atoms in their ground state. That is, $\epsilon_{gs,H} = 0$.

In the temperature range $1000 K \leq T \leq 2000 K$, we have $\theta_r \ll T \ll \theta_v$ (see Table 11.2 on p. 253), so only the rotational modes of the H_2 molecule are unfrozen. According to RB eq. (11.31), we have

$$Z_{H_2(int)} = 2^2 \frac{1}{2} \left(\frac{T}{\theta_r} \right) e^{-\epsilon_{gs,H_2}/kT}$$

where $\epsilon_{gs,H_2} = -4.476 \text{ eV}$ [see Table 11.2 again]

Thus,

$$K(T) = \lambda_H^{-6} \lambda_{H_2}^3 \frac{(4)^2}{(2)^2 \frac{1}{2} \frac{T}{\theta_r} e^{-\epsilon_{gs,H_2}/kT}}$$

Recalling that $\lambda = \sqrt{\frac{2\pi m k^2}{m k T}}$,

$$K(T) = \left(\frac{2\pi k^2}{kT} \right)^{-3/2} \frac{m_H^3}{m_{H_2}^{3/2}} \frac{8\theta_r}{T} e^{\epsilon_{gs,H_2}/kT}$$

Putting $m_{H_2} \approx 2m_H$,

$$K(T) = \left(\frac{2\pi k^2}{m_H kT} \right)^{-3/2} \frac{4\theta_r}{\sqrt{2} T} e^{\epsilon_{gs,H_2}/kT}$$

$$= \left[\frac{2\pi (1.055 \times 10^{-34} \text{ J}\cdot\text{s})^2}{(1.674 \times 10^{-27} \text{ kg}) (1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1})} \right]^{-3/2} \times \frac{4}{\sqrt{2}} (87.5 \text{ K}) T^{1/2} \exp\left(\frac{-4.476 \text{ eV}}{T (8.617 \times 10^{-5} \text{ eV/K})} \right)$$

Examining the units carefully, we see that the quantity raised to the $-3/2$ power has units of $\text{m}^{-3} \text{K}^{-3/2}$.

$$K(T) = (1.90 \times 10^{26} \text{ m}^{-3} \text{K}^{-3/2}) \frac{4}{\sqrt{2}} (87.5 \text{ K}) T^{1/2} \times \exp\left(\frac{-5.19 \times 10^4 \text{ K}}{T} \right)$$

9

That is,

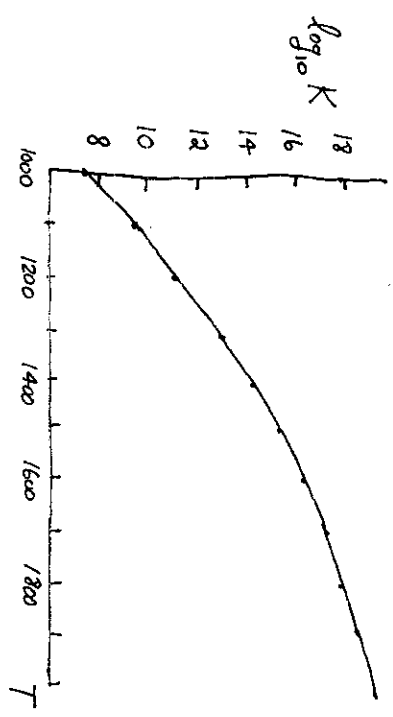
$$K(T) = (4.70 \times 10^{28} \text{ m}^{-3}) T^{1/2} \exp\left(\frac{-5.19 \times 10^4 \text{ K}}{T}\right)$$

where T is given in degrees Kelvin.

Let us tabulate the numerical values:

| T | K(T) |
|--------|--------------------------------------|
| 1000 K | $4.29 \times 10^7 \text{ m}^{-3}$ |
| 1100 K | $5.03 \times 10^9 \text{ m}^{-3}$ |
| 1200 K | $2.68 \times 10^{11} \text{ m}^{-3}$ |
| 1300 K | $7.77 \times 10^{12} \text{ m}^{-3}$ |
| 1400 K | $1.40 \times 10^{14} \text{ m}^{-3}$ |
| 1500 K | $1.71 \times 10^{15} \text{ m}^{-3}$ |
| 1600 K | $1.54 \times 10^{16} \text{ m}^{-3}$ |
| 1700 K | $1.07 \times 10^{17} \text{ m}^{-3}$ |
| 1800 K | $5.99 \times 10^{17} \text{ m}^{-3}$ |
| 1900 K | $2.81 \times 10^{18} \text{ m}^{-3}$ |
| 2000 K | $1.13 \times 10^{19} \text{ m}^{-3}$ |

Graphically,



10

(b) Let

$$f = \frac{[H]}{[H] + [H_2]}$$

From part (a),

$$\frac{[H]^2}{[H_2]} = K(T)$$

We are given $[H] + 2[H_2] \equiv A = 2.5 \times 10^{15} \text{ m}^{-3}$.

Let $x = [H]$, $y = [H_2]$. Then,

$$f = \frac{x}{x+y} \tag{1}$$

$$\frac{x^2}{y} = K(T) \tag{2}$$

$$x+2y = A \tag{3}$$

From (a), $y = \frac{x^2}{K(T)}$. Insert this in (1) to get

$$f = \frac{x}{x + \frac{x^2}{K(T)}} = \frac{1}{1 + \frac{x}{K(T)}} \tag{4}$$

From (3), $y = \frac{A-x}{2}$, Insert this in (2) to get

$$x^2 = yK(T) = \frac{1}{2}(A-x)K(T)$$

Thus, $x^2 + \frac{1}{2}xK(T) - \frac{1}{2}AK(T) = 0$

Solve the quadratic equation:

$$x = \frac{1}{2} \left[-\frac{1}{2}K(T) + \sqrt{\left[\frac{1}{4}K(T)\right]^2 + 2AK(T)} \right]$$

where we have chosen the positive root since x is known to be positive.

Thus,

$$\frac{x}{K(T)} = -\frac{1}{4} + \frac{1}{2} \sqrt{\frac{1}{4} + \frac{2A}{K(T)}} = -\frac{1}{4} \left[1 - \sqrt{1 + \frac{8A}{K(T)}} \right]$$

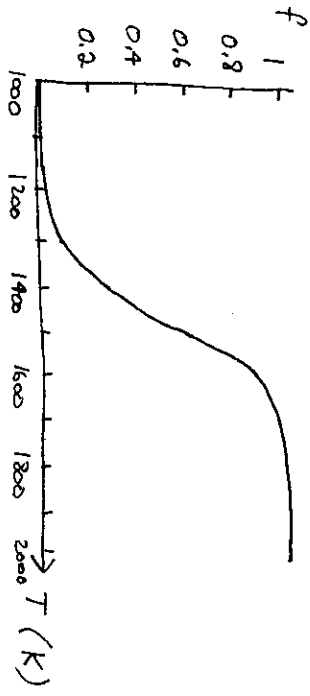
and plugging back in (4) yields

$$f = \frac{1}{\frac{3}{4} + \frac{1}{4} \sqrt{1 + \frac{8A}{K(T)}}}$$

Using the table of values for $K(T)$ and $A = 2.5 \times 10^{15} \text{ m}^{-3}$

| T (°K) | f |
|--------|-----------------------|
| 1000 | 1.85×10^{-4} |
| 1100 | 2.00×10^{-3} |
| 1200 | 1.45×10^{-2} |
| 1300 | 7.44×10^{-2} |
| 1400 | 0.267 |
| 1500 | 0.609 |
| 1600 | 0.886 |
| 1700 | 0.978 |
| 1800 | 0.996 |
| 1900 | 0.999 |
| 2000 | 0.9998 |

Graphically,



(c) To obtain the temperature corresponding to $f = 0.8$, use linear extrapolation on the table of numbers above:

| T | f |
|------|-------|
| 1500 | 0.609 |
| X | 0.8 |
| 1600 | 0.886 |

To find the unknown X, use the fact that the slope of the line connecting these three points is given by:

$$\frac{0.8 - 0.609}{x - 1500} = \frac{0.888 - 0.8}{1600 - x}$$

That is

$$0.086(x - 1500) = 0.191(1600 - x)$$

$$0.277x = 434.6$$

$$x = 1569$$

Thus, we estimate that $f = 0.8$ at $T = 1569$ K.

This should be compared with characteristic molecular temperatures defined by $(k_B \text{ dissociation energy}) / k_B$. This temperature is:

$$\frac{4.476 \text{ eV}}{8.617 \times 10^{-5} \text{ eV/K}} = 5.19 \times 10^4 \text{ K}$$

which is clearly significantly larger than 1569 K.

That is, already at temperatures that are as small as 3% of the characteristic molecular dissociation temperature, we find that the dissociation fraction of atomic hydrogen is 80% at equilibrium in the reaction $H_2 \rightleftharpoons 2H$.

④ RB Chapter 11, problem 15

The reaction of relevance is $\gamma + \gamma \leftrightarrow e^- + e^-$. Thermal and diffusive equilibrium implies that the chemical potentials satisfy

$$-2\mu_\gamma + \mu_{e^-} + \mu_{e^-} = 0$$

We know that $\mu_\gamma = 0$. Using RB eq. (11.56) on p. 263

$$\mu_{e^-} = m_e c^2 - k_B T \ln \left(\frac{2(2\pi k_B T)^{-3/2}}{N_{e^-}} \right)$$

[Note: There is an obvious typographical error in the textbook. Dimensional analysis tells you that $m_e c$ should be replaced by $m_e c^2$ since μ has units of an energy.]

Similarly,

$$\mu_{e^+} = m_e c^2 - k_B T \ln \left(\frac{2(2\pi k_B T)^{-3/2}}{N_{e^+}} \right)$$

Charge conservation implies that $N_{e^-} = N_{e^+}$. Thus, $\mu_{e^-} = \mu_{e^+}$. Plugging this result into the equation at the top of the page (along with $\mu_\gamma = 0$) implies that $\mu_{e^-} = \mu_{e^+} = 0$. Thus,

$$m_e c^2 = k_B T \ln \left(\frac{2(2\pi k_B T)^{-3/2}}{N} \right)$$

where $N = N_{e^-} = N_{e^+}$. Solving for $\frac{N}{V}$, using $k_B = \sqrt{\frac{2\pi k_B^2}{m_e k_B T}}$,

$$\frac{N}{V} = 2 \left(\frac{2\pi k_B^2}{m_e k_B T} \right)^{-3/2} \exp \frac{-m_e c^2}{k_B T}$$

(15)

At $T = 10^8 \text{ K}$,

$$\frac{N}{V} = 2 \left[\frac{2\pi(1.055 \times 10^{-34} \text{ J}\cdot\text{s})^2}{(9.109 \times 10^{-31} \text{ kg})(1.381 \times 10^{-23} \text{ J/K})(10^8 \text{ K})} \right]^{-3/2} \\ \times \exp \left[\frac{-(9.109 \times 10^{-31} \text{ kg})(2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})^2}{(1.381 \times 10^{-23} \text{ J/K})(10^8 \text{ K})} \right] \\ = (4.825 \times 10^{23} \text{ m}^{-3}) \exp(-59.28) \\ = 8.64 \times 10^7 \text{ m}^{-3}$$

That is an impressive number density of electrons!

(16)

⑤ RB Chapter 12, problem 3

(a) The chemical potential is given by

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}$$

$$\text{where } F = -kT \ln Z$$

We can express the partition function for N atoms in terms of the partition function for one atom:

$$Z = Z_1^N$$

(There is no $\frac{1}{N!}$ here since the atoms of a solid are spatially localized

in the lattice, so there is no question of indistinguishability.)

Hence,

$$Z_1 = \sum_r e^{-\epsilon_r/kT}$$

and the energy levels are those of a three-dimensional harmonic oscillator. We can write

$$\epsilon_r = -\epsilon_0 + (n_x + n_y + n_z) h\nu_0$$

where n_x, n_y and n_z are any non-negative integer, and $-\epsilon_0$ is the binding energy per atom relative to the gas phase (which will include any zero-point energies as well). Thus,

$$Z_1 = e^{\epsilon_0/kT} \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} e^{-n_x h\nu_0/kT} e^{-n_y h\nu_0/kT} e^{-n_z h\nu_0/kT}$$

Each sum is evaluated independently, using:

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

Thus, we obtain

$$Z_1 = \frac{e^{\epsilon_0/kT}}{(1 - e^{-\epsilon_0/kT})^3}$$

Now,

$$F = -kT \ln Z_1^N = -NkT \ln Z_1,$$

and

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -kT \ln Z_1,$$

Thus, for the solid,

$$\mu_s = -\epsilon_0 + 3kT \ln(1 - e^{-\epsilon_0/kT})$$

(b) We next consider the chemical potential of the gas phase, μ_g . Using the ideal gas approximation, we can use RB eq (7.20) on p.157:

$$\mu_g = -kT \ln \left[\frac{V}{N} \lambda_{th}^{-3} \right]$$

When the gas and the solid are in equilibrium along the sublimation curve, $\mu_g = \mu_s$

Thus,

$$-kT \ln \left[\frac{V}{N} \lambda_{th}^{-3} \right] = -\epsilon_0 + 3kT \ln(1 - e^{-\epsilon_0/kT})$$

where the subscript g refers to the gas. Using the ideal gas law, $P_g V = N_g kT$, so we can write:

$$-kT \ln \left[\frac{kT}{P_g} \lambda_{th}^{-3} \right] = -\epsilon_0 + 3kT \ln(1 - e^{-\epsilon_0/kT})$$

Solving for P_g ,

$$\ln \left(\frac{kT}{P_g} \lambda_{th}^{-3} \right) = \frac{\epsilon_0}{kT} - 3 \ln(1 - e^{-\epsilon_0/kT})$$

Exponentiating,

$$\frac{kT}{P_g} \lambda_{th}^{-3} = e^{\epsilon_0/kT} \frac{1}{(1 - e^{-\epsilon_0/kT})^3}$$

Thus,

$$P_g = kT \lambda_{th}^{-3} e^{\epsilon_0/kT} (1 - e^{-\epsilon_0/kT})^3$$

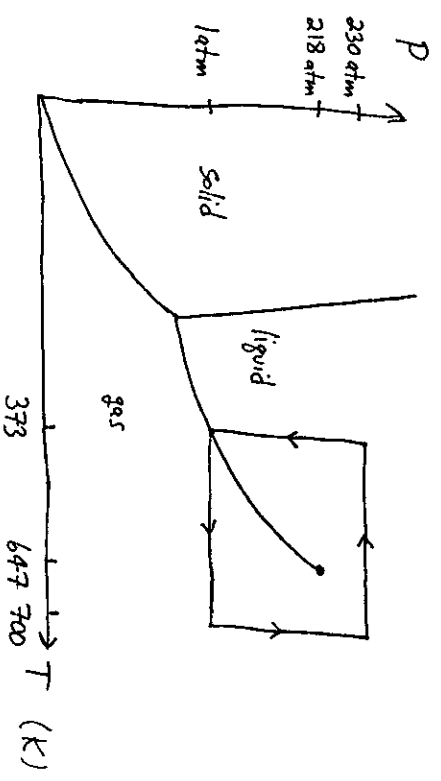
(c) In the limit of $kT \gg \epsilon_0$, $1 - e^{-\epsilon_0/kT} \approx \frac{\epsilon_0}{kT}$. [Using $1 - e^{-x} \approx 1 - (1-x) = x$]. Thus,

$$P_g = kT \lambda_{th}^{-3} \left(\frac{\epsilon_0}{kT} \right)^3 e^{-\epsilon_0/kT}$$

where $\lambda_{th} \equiv \frac{h}{\sqrt{2\pi m kT}}$

RB Chapter 12, problem 4

(a) If we draw the path of the various processes on a P vs. T graph, we would find:



Although not drawn to scale, we note that the critical point corresponds to $T = 647\text{ K}$ and $P = 218\text{ atm}$. Thus, the path drawn above, which starts at $P = 1\text{ atm}$ and $T = 373\text{ K}$ in the gas phase and ends up in the liquid phase (at the same values of P and T), never crosses a phase transition line.

The net change in the system's energy is independent of path. Thus, we can obtain the desired result simply by choosing a more convenient path — namely, starting with gas at $P = 1\text{ atm}$ and $T = 373\text{ K}$, simply convert all the gas to liquid at fixed P and T . The change in energy in this process is simply $-LN$, where L is the latent heat of transformation for the liquid to gas phase transformation, and N is the number of H_2O molecules. Note the sign. The energy is reduced when converting gas to liquid.

According to Table 12.2 on p374 of RB, $L = 0.47\text{ eV/molecule}$ for the liquid to gas phase transformation of H_2O . Thus, for $N = 10^{24}$ molecules, the net change in the energy of the system

is $-0.47 \times 10^{24}\text{ eV} = 6.73 \times 10^4\text{ J}$.

(b) On the vaporization curve, which is a coexistence curve, the chemical potentials of liquid and gas are equal. Thus, the net change in the chemical potential of H_2O in the process described above is zero.

(21)

7) RB Chapter 12, problem 6

(a) The vapor pressure of solid ammonia is

$$\ln P = 16.27 - \frac{3729}{T}$$

The vapor pressure of liquid ammonia is

$$\ln P = 12.79 - \frac{3049}{T}$$

These two lines intersect at the triple point. Thus,

$$16.27 - \frac{3729}{T} = 12.79 - \frac{3049}{T}$$

$$3.48 = \frac{680}{T}$$

$$T = 195.4 \text{ K}$$

Insert this value of T in either of the equations for $\ln P$:

$$\ln P = -2.8137$$

$$P = 6.00 \times 10^{-2} \text{ atm}$$

(b) Use the Clausius-Clapeyron equation, and assume that $V_g \gg V_l, V_s$. In addition, assume that the ideal gas law can be used to express $V_g = \frac{RT}{P}$. Then,

$$\frac{1}{P} \frac{dP}{dT} = \frac{L_{\text{vap}}}{RT^2} \quad [\text{RB eq (12.29) on p 281}]$$

where L_{vap} is the latent heat of vaporization.

(22)

Using the equation for the vaporization curve:

$$\ln P = 12.79 - \frac{3049 \text{ K}}{T}$$

we have

$$\frac{d}{dT} \ln P = \frac{3049 \text{ K}}{T^2}$$

Since $\frac{d}{dT} \ln P = \frac{1}{P} \frac{dP}{dT}$, we conclude that

$$\begin{aligned} L_{\text{vap}} &= RT^2 \frac{d}{dT} \ln P = (3049 \text{ K}) k \\ &= (3049 \text{ K}) (8.617 \times 10^{-5} \text{ eV/K}) \\ &= 0.2627 \text{ eV} \end{aligned}$$

This is the heat of vaporization per molecule.

(c) By definition,

$$L_{\text{vap}} = T(S_g - S_l)$$

$$L_{\text{fusion}} = T(S_l - S_s)$$

$$L_{\text{sublimation}} = T(S_g - S_s)$$

Thus, it is obvious that

$$L_{\text{sublimation}} = L_{\text{vap}} + L_{\text{fusion}}$$

Given $L_{\text{sublimation}} = 0.3214 \text{ eV/molecule}$ and using the results of part (b), we obtain

$$L_{\text{fusion}} = 0.3214 - 0.2627 = 0.0587 \text{ eV/molecule.}$$