

# Problem Set 3

①

	$^2S_{1/2}$	$^2P_{3/2, 1/2}$	$^2D_{5/2, 3/2}$
g	2	6	10
E	0	$14904 \text{ cm}^{-1}$	$27206 \text{ cm}^{-1}$

$$q_{elec} = \sum_i^{elec \text{ states}} g_i e^{-E_i/kT} \quad \left( 6933 \frac{\text{K}}{\text{cm}^{-1}} \right)$$

$$= 2 + 6 e^{-\frac{14904 \times 6933}{T}} + 10 e^{-\frac{27206 \times 6933}{T}} \approx 2$$

$$q_{transl} = \left( \frac{2\pi m k T}{h^2} \right)^{3/2} V$$

$$V = 8.2054 \times 10^{-5} \text{ T m}^3 \text{ mole}^{-1}$$

1 atom, 1 mole

$$q_{transl} = \left[ \frac{2\pi \cdot 1.38066 \times 10^{-23} \text{ J K}^{-1} \cdot 1.6606 \times 10^{-27} \text{ kg/amu}}{(6.62618 \times 10^{-34} \text{ Js})^2} \right]^{3/2} \cdot 8.2054 \times 10^{-5} \text{ T m}^3 \text{ amu}^{-3/2}$$

$$= 1.5421 \times 10^{22} \text{ T}^{5/2} \text{ m}^{3/2} \text{ K amu}$$

	I	$g_{nuc \text{ spin}}$	$q_{elec}$	m	T	$q_{transl}$
6Li	1	3	2	6.017034	1000 1500	$7.1976 \times 10^{30}$ $1.9834 \times 10^{31}$
7Li	3/2	4	2	7.018232	1000 1500	$9.0668 \times 10^{30}$ $2.4985 \times 10^{31}$

T	$\frac{q_i}{N_{\text{avo}}}$	$\frac{q_{\text{elec}}}{g_{\text{mol}}}$	fractional abundance	average $\frac{q}{N_{\text{avo}}}$	ANSWER: $S/J\text{mol}^{-1}K^{-1}$
1000	$7.1712 \times 10^7$	} ${}^6\text{Li}$	0.0752	$1.1678 \times 10^8$	175.23
1500	$1.9762 \times 10^8$			$3.2182 \times 10^8$	183.66
1000	$1.2045 \times 10^8$	} ${}^7\text{Li}$	0.9248		
1500	$3.3192 \times 10^8$				

$$S = kN \ln \frac{q}{N} + \frac{E}{T} + kN = R \left[ \ln \frac{q}{N} + \frac{E}{2} \right]$$

since  $E = E_{\text{transl}} + E_{\text{int}} \approx \frac{3}{2} RT$  high T limit is good here

where  $R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$

If we had used pure  ${}^7\text{Li}$  we would have arrived at  $S = 175.49$  at 1000K and 183.92 at 1500K not very different from the averaged values of 175.23 and 183.66

② Actually should do

$$(.0752)^2 S({}^6\text{Li}) + (.9248)^2 S({}^7\text{Li}) + 2(.0752)(.9248) S({}^6\text{Li} {}^7\text{Li})$$

but as seen above, the difference is small, so let us do only  ${}^7\text{Li}_2$

$$I = \mu r_e^2$$

$$\mu = \frac{7.018232}{2}, r_e = 2.672 \times 10^{-8} \text{ cm}$$

$$y = \frac{h^2}{2IkT} = \frac{(1.0546 \times 10^{-34} \text{ Js})^2 \times 6.02204 \times 10^{26}}{T \cdot 7.018232 \times (2.672 \times 10^{-10})^2 \cdot 1.38066 \times 10^{-23} \text{ JK}^{-1}}$$

$$= 0.9681/T$$

$g_{trans} g_{elec} g_{vib} g_{rot} g_{nuc\ spin}$

$m = 2 \times 7.018232$  again  $V = 8.2057 \times 10^{-5} T^3 \text{ m}^3 \text{ mol}^{-1}$   
1 atm  
1 mol

$$g_{trans} = \left[ \frac{2\pi \cdot 1.38066 \times 10^{-23} \text{ JK}^{-1} \times 1.6606 \times 10^{-27} \text{ kg} \times 2 \times 7.018232 \text{ amu}}{(6.62618 \times 10^{-34} \text{ Js})^2} \right]^{3/2} \cdot \frac{8.2057 \times 10^{-5}}{T^{3/2}}$$

$g_{trans} = 8.1095 \times 10^{23} T^{5/2}$

ground state is  $^1\Sigma_g^+$

$$g_{elec} = 1 + 1 \cdot e^{-\frac{14068 \times 0.6933}{T}} + 2 \cdot e^{-\frac{20439 \times 0.6933}{T}} + 1 \cdot e^{-\frac{30558 \times 0.6933}{T}}$$

$\approx 1$

Use the high temperature limit for  $g_{vib}$ :

$g_{vib} = \frac{1}{1 - e^{-u}}$ ,  $u = \frac{h\nu}{kT}$   $\omega_e = 351.43 \text{ cm}^{-1}$

$$\frac{6.62618 \times 10^{-34} \text{ Js} \times 2.9979 \times 10^{10} \text{ cm}^{-1}}{1.38066 \times 10^{-23} \text{ JK}^{-1}} \times 351.43 \text{ cm}^{-1} = 505.64 \text{ K}^{-1}$$

$u = 505.64/T$

$g_{vib} = \frac{1}{1 - e^{-\frac{505.64}{T}}}$

$^7\text{Li}$  are fermions  $I = 3/2$   
 $g_{rot} g_{nuc\ spin} (I+1)(2I+1) = 10$  ortho  
 $I(2I+1) = 6$  para

For  $^1\Sigma_g^+$  symmetric with respect to interchange of nuclei therefore  $J_{odd}$  must go with ortho so that total wavefunction is anti-symmetric with respect to  $P_{AB}$

~~10~~  $J=1$  ortho  
~~6~~  $J=0$  para

Separate sums:

$$q_{\text{fund spin}} = \sum_{\text{Even}} (2J+1) e^{-\frac{0.9681 J(J+1)}{T}} + 10 \sum_{\text{Odd}} (2J+1) e^{-\frac{0.9681 J(J+1)}{T}}$$

actually the high temperature limit is good enough so

use  $q_{\text{fund spin}} = (2I+1)^2 \frac{1}{2} = \frac{8}{2} = \frac{8T}{0.9681} = 8.2636T$

↑  
symmetry number

$$q = q_{\text{trans}} \cdot q_{\text{elec}} \cdot q_{\text{vib}} \cdot q_{\text{rot}} \cdot q_{\text{fund spin}}$$

$$= 8.1095 \times 10^{23} T^{5/2} \cdot 1 \cdot \frac{1}{1 - e^{-\frac{505.64}{T}}} \cdot 8.2636T$$

$$\frac{q}{N} = \frac{11.128 T^{3/2}}{1 - e^{-\frac{505.64}{T}}} = 8.8666 \times 10^{11} \text{ at } 1000 \text{ K}$$

$$= 5.0831 \times 10^{12} \text{ at } 1500 \text{ K}$$

$T / K$	$\frac{q_{\text{trans}}}{N}$	$q_{\text{int}}$	$\frac{q}{N}$	$\ln \left( \frac{q}{N} \right)$	ANSWERS: $S$
1000 K	$4.2584 \times 10^7$	$2.0821 \times 10^4$	$8.8666 \times 10^{11}$	27.511	266.15
1500 K	$1.1735 \times 10^8$	$4.3317 \times 10^4$	$5.0831 \times 10^{12}$	29.257	280.67

as before, we used

$$S = R \left[ \ln \frac{q}{N} + \frac{q}{2} \right], \quad R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$E = E_{\text{trans}} + E_{\text{int}} = \frac{3}{2} RT + RT + RT \approx \frac{7}{2} RT$$

normally  $q_{\text{fund spin}}$

trans      rot      vib (approx)

↑  
How good is this?

$$N h \nu_e = 6.622 \times 10^{-34} \text{ Js} \times 2.99792 \times 10^{10} \text{ cm}^{-1} \times 351.43 \text{ cm}^{-1}$$

$$= 4204 \text{ J}$$

$RT = 8314 \text{ J at } 1000 \text{ K}$  and  $1.2472 \times 10^4 \text{ at } 1500 \text{ K}$

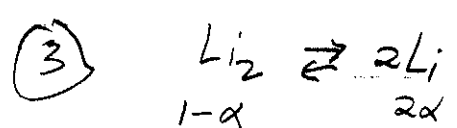
$$E_{\text{vib}} = N \langle E_{\text{vib}} \rangle = N h \nu_e \langle v + \frac{1}{2} \rangle$$

where  $\langle v + \frac{1}{2} \rangle = \sum_{v=0}^{\infty} (v + \frac{1}{2}) e^{-u(v+\frac{1}{2})}$

$$= \frac{1}{2} \frac{e^{u/2} + e^{-u/2}}{e^{u/2} - e^{-u/2}}$$

	$\frac{e^{u/2} + e^{-u/2}}{e^{u/2} - e^{-u/2}}$	$E_{\text{vib}}$	$RT$	$\frac{E_{\text{vib}}}{T}$
1000	4.03923	8498.5 J	8314 J	1.021 R
1500	5.9892	12589.3 J	12472 J	1.0094 R

$\therefore E_{\text{vib}} \approx RT$  is close enough



Fraction in the vapor which are in the form of  $\text{Li}_2 = \frac{1-\alpha}{1+\alpha}$

mole fraction  $\frac{1-\alpha}{1+\alpha}$  and  $\frac{2\alpha}{1+\alpha}$

$$K_p = \frac{(P_{\text{Li}})^2}{P_{\text{Li}_2}} = \frac{(\frac{2\alpha P}{1+\alpha})^2}{\frac{1-\alpha P}{1+\alpha}} = \frac{4\alpha^2 P}{1-\alpha^2}$$

0.782 mmHg at  $T = 1000 \text{ K}$

$$\Delta D_0 = -D_0(\text{Li}_2) = -1.08 \pm 0.05 \text{ eV}$$

$$-\frac{D_0}{kT} = \frac{-1.08 \text{ eV} \times 1.602192 \times 10^{-19} \text{ J}}{1.38066 \times 10^{-23} \text{ J K}^{-1} \times 1000 \text{ K}} = -12.533$$

We have previously derived:

$$K_p = \frac{\left(\frac{q_{Li}}{N}\right)^2 e^{-D_0/kT}}{\frac{q_{Li_2}}{N}}$$

Using  ${}^7\text{Li}$  results from problems 1 and 2,

$$K_p = \frac{(1.2045 \times 10^8)^2 e^{-12.533}}{8.8666 \times 10^{11}} = 5.90 \times 10^{-2}$$

$$-RT \ln K_p = 2.3532 \times 10^4 \text{ J}$$

$$5.90 \times 10^{-2} = \frac{4\alpha^2}{1-\alpha^2} \left(\frac{0.782}{760}\right) \quad \alpha^2 = 0.93479$$

$$\alpha = 0.96685$$

$$\frac{1-\alpha}{1+\alpha} = 1.6857 \times 10^{-2} \quad \text{ANSWER}$$

$$\Delta G = \Delta H - T\Delta S \quad (\text{for } {}^7\text{Li only})$$

$$\Delta S = [2 \times 175.49 - 266.15] = 84.83 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H = \Delta E + RT \frac{\Delta n}{2-1} \quad \text{ideal gas assumption}$$

$$\Delta E = [2\left(\frac{3}{2}RT\right) - \left(\frac{7}{2}RT - D_0\right)] \text{ from problems 1 \& 2}$$

$$\Delta H = \frac{1}{2}RT + D_0 = RT\left(\frac{1}{2} + 12.533\right) = 108361.7 \text{ J mol}^{-1}$$

$$\Delta G = 108361.7 \text{ J mol}^{-1} - 84.83 \times 10^3 = 23531.7$$

$$= -RT \ln K_p$$

$$\ln K_p = -2.8302$$

$K_p = 0.0590$  which is the same of course as that found earlier

→ Discussion to verify S is correct and using  $D_0$  was okay

$$G_{\text{prod}} = 2G_{\text{Li}} = 2 \left[ -RT \ln \frac{q_{\text{Li}}}{N} \right]$$

$$G_{\text{react}} = G_{\text{Li}_2} = -RT \left( \ln \frac{q_{\text{Li}_2}}{N} + \frac{D_0}{RT} \right)$$

explicitly so that  $q$  is based on same energy zero.

$$\Delta G = G_{\text{prod}} - G_{\text{react}} = 2G_{\text{Li}} - G_{\text{Li}_2}$$

$$= -RT \left\{ 2 \ln \left( \frac{q_{\text{Li}}}{N} \right) - \left[ \ln \frac{q_{\text{Li}_2}}{N} + \frac{D_0}{RT} \right] \right\}$$

$$= -RT \ln \frac{\left( \frac{q_{\text{Li}}}{N} \right)^2}{\frac{q_{\text{Li}_2}}{N}} e^{-D_0/RT}$$

$$E_{\text{prod}} = 2E_{\text{Li}} = 2 \left[ \frac{3}{2} RT \right]$$

relative to ground state atoms defined as  $E=0$

$$E_{\text{react}} = E_{\text{Li}_2} = \frac{1}{2} RT - D_0$$

relative to ground state. Atoms defined as  $E=0$

$$S_{\text{prod}} = 2S_{\text{Li}} = 2 \left[ R \ln \frac{q_{\text{Li}}}{N} + \frac{E_{\text{Li}}}{T} + R \right]$$

$$S_{\text{react}} = S_{\text{Li}_2} = R \left( \ln \frac{q_{\text{Li}_2}}{N} + \frac{D_0}{RT} \right) + \frac{E_{\text{Li}_2}}{T} + R$$

explicitly so that  $q$  is based on same energy zero

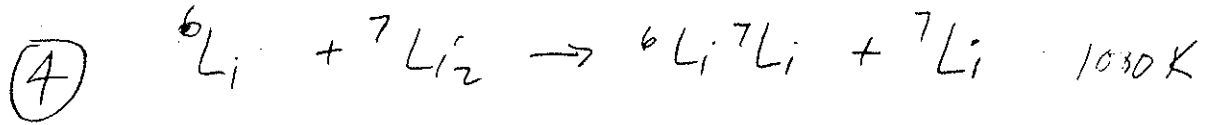
$$H_{\text{prod}} = 2H_{\text{Li}} = 2 \left[ E_{\text{Li}} + RT \right]$$

ideal gas assumed

$$H_{\text{react}} = H_{\text{Li}_2} = E_{\text{Li}_2} + RT$$







As we have derived in class

$$K = \frac{(1 - e^{-u}) u' e^{-u'/2}}{(1 - e^{-u'}) u e^{-u'/2}}$$

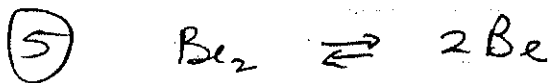
$$\text{where } u = \frac{1.4388 \text{ W}_e({}^7\text{Li}_2)}{T} \quad u' = \frac{1.4388 \text{ W}_e({}^7\text{Li}{}^6\text{Li})}{T}$$

$\uparrow$   
 $351.43 \text{ cm}^{-1}$

$$\text{W}_e({}^7\text{Li}{}^6\text{Li}) = 351.43 \times \frac{\mu({}^7\text{Li}_2)}{\mu({}^7\text{Li}{}^6\text{Li})} = 380.67 \text{ cm}^{-1}$$

$$u = 0.5056 \quad u' = 0.5477 \quad \text{Substitute into above expression}$$

$$K = 0.9982$$



(to be added later)

6. Partition function for the system is

$$q = g_1 e^{-E_1/kT} + g_2 e^{-E_2/kT}$$

The fraction of molecules with energy  $E_1$  is

$$N_1 = \frac{N}{q} g_1 e^{-E_1/kT}$$

The fraction of molecules with energy  $E_2$  is

$$N_2 = \frac{N}{q} g_2 e^{-E_2/kT}$$

Energy is  $E = \sum_i N_i E_i = N_1 E_1 + N_2 E_2$

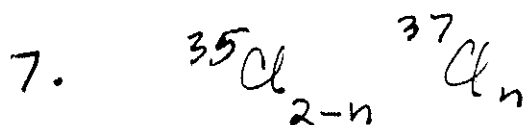
$$\begin{aligned} &= \frac{N}{q} [g_1 E_1 e^{-E_1/kT} + g_2 E_2 e^{-E_2/kT}] \\ &= N \frac{[g_1 E_1 e^{-E_1/kT} + g_2 E_2 e^{-E_2/kT}]}{g_1 e^{-E_1/kT} + g_2 e^{-E_2/kT}} \end{aligned}$$

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = N \left[ \frac{1}{q} \left( g_1 E_1 e^{-E_1/kT} \cdot \frac{E_1}{kT^2} + g_2 E_2 e^{-E_2/kT} \cdot \frac{E_2}{kT^2} \right) - \frac{1}{q^2} \left( g_1 E_1 e^{-E_1/kT} + g_2 E_2 e^{-E_2/kT} \right) \frac{dq}{dT} \right]$$

$$\text{but } \frac{dq}{dT} = g_1 e^{-E_1/kT} \cdot \frac{E_1}{kT^2} + g_2 e^{-E_2/kT} \cdot \frac{E_2}{kT^2}$$

$$C_V = \frac{N}{kT^2} g_2 \left[ (g_1 E_1^2 e^{-E_1/kT} + g_2 E_2^2 e^{-E_2/kT}) (g_1 e^{-E_1/kT} + g_2 e^{-E_2/kT}) - (g_1 E_1 e^{-E_1/kT} + g_2 E_2 e^{-E_2/kT}) (g_1 e^{-E_1/kT} + g_2 e^{-E_2/kT}) \right]$$

$$\begin{aligned}
C_V &= \frac{N}{kT^2 g^2} \left[ \begin{aligned} & \left( \cancel{g_1^2 \epsilon_1^2} - \cancel{g_1^2 \epsilon_1^2} \right) e^{-2\epsilon_1/kT} \\ & + \left( \cancel{g_2^2 \epsilon_2^2} - \cancel{g_2^2 \epsilon_2^2} \right) e^{-2\epsilon_2/kT} \\ & + \left( g_1 g_2 \epsilon_2^2 \right) e^{-(\epsilon_1 + \epsilon_2)/kT} \\ & + \left( g_1 g_2 \epsilon_1^2 \right) e^{-(\epsilon_1 + \epsilon_2)/kT} \\ & - \left( g_1 g_2 \epsilon_1 \epsilon_2 \right) e^{-(\epsilon_1 + \epsilon_2)/kT} \\ & + \left( g_1 g_2 \epsilon_1 \epsilon_2 \right) e^{-(\epsilon_1 + \epsilon_2)/kT} \end{aligned} \right] \\
&= \frac{N g_1 g_2}{kT^2 g^2} \left[ \underbrace{\epsilon_2^2 + \epsilon_1^2 - 2\epsilon_1 \epsilon_2}_{(\epsilon_2 - \epsilon_1)^2} \right] e^{-(\epsilon_1 + \epsilon_2)/kT} \\
&= \frac{N}{kT^2} \frac{g_1 e^{-\epsilon_1/kT}}{g} \cdot \frac{g_2 e^{-\epsilon_2/kT}}{g} \cdot (\epsilon_2 - \epsilon_1)^2 \\
&= \frac{N}{kT^2} \frac{N_1}{N} \frac{N_2}{N} (\epsilon_2 - \epsilon_1)^2 \\
&= \frac{N_1 N_2 (\epsilon_2 - \epsilon_1)^2}{N kT^2}
\end{aligned}$$



Probability of getting this particular isotopomer

is  $\frac{2!}{n!(2-n)!} \underbrace{(.25)^n}_{\text{probability of picking } ^{37}\text{Cl} \text{ is } 0.25 \text{ each time } \text{Do it } n \text{ times}} \underbrace{(.75)^{2-n}}_{\text{probability of picking } ^{35}\text{Cl} \text{ is } 0.75 \text{ for each time } \text{Do it } (2-n) \text{ times}}$

no. of ways of picking  $n$  heavy atoms out of 2 in the molecule

probability of picking  $^{35}\text{Cl}$  is 0.75 for each time. Do it  $(2-n)$  times

probability of picking  $^{37}\text{Cl}$  is 0.25 each time. Do it  $n$  times

$^{35}\text{Cl} \ ^{35}\text{Cl} \ n=0 \quad \frac{2!}{0!(2-0)!} (.25)^2 (.75)^0 = 0.0625$

$^{35}\text{Cl} \ ^{37}\text{Cl} \ n=1 \quad \frac{2!}{1!(2-1)!} (.25)^1 (.75)^1 = 2 \times .1875 = .375$

$^{37}\text{Cl} \ ^{37}\text{Cl} \ n=2 \quad \frac{2!}{2!(2-2)!} (.25)^0 (.75)^2 = 0.5625$

Total = 1.0 as should be

In general if  $N$  replaceable <sup>hydrogen</sup> atoms for example and the deuterium fraction is  $d$ , that is 100 atoms of D out of 100 atoms of  $(\text{H} + \text{D})$  the fraction of isotopomer

$\text{XH}_{N-n} \text{D}_n$  is given by

$$\frac{N!}{n!(N-n)!} (d)^n (1-d)^{N-n}$$

8. For the reaction  $I_2(g) \rightleftharpoons 2I(g)$

$$K_p = \frac{(N_I)^2}{N_{I_2}} \cdot \frac{kT}{V}$$

Let  $N_I$  = no. of I atoms  
 $N_{I_2}$  = no. of  $I_2$  molec.

$$p = \frac{NkT}{V} \text{ ideal gas}$$

$$p_I = \frac{N_I kT}{V} \quad p_{I_2} = \frac{N_{I_2} kT}{V}$$

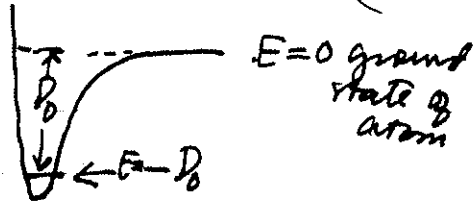
$$\frac{(N_I)^2}{N_{I_2}} = \frac{(q_I)^2}{q_{I_2}}$$

$$q = \sum_i g_i e^{-\epsilon_i/kT} V$$

$$q_I = q_{\text{trans}} \cdot q_{\text{elec}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \cdot q_{\text{spin}}$$

$$= \left( \frac{2\pi m kT}{h^2} \right)^{3/2} V \cdot 4 \cdot (2I_A + 1)$$

elec. degeneracy =  $2J+1$   
 for  $J=3/2$   
 only ground elec. state  $\epsilon_i=0$



$$q_{\text{vib}} = \sum_{v=0}^{\infty} 1 \cdot e^{-v h \nu / kT}$$

= infinite series with a known sum

$$= \frac{1}{1 - e^{-h\nu/kT}}$$

$$q_{I_2} = q_{\text{trans}} \cdot q_{\text{elec}} \cdot q_{\text{vib}} \cdot q_{\text{rot}} \cdot q_{\text{spin}}$$

$$= \left( \frac{2\pi \cdot 2m kT}{h^2} \right)^{3/2} V \cdot 1 \cdot e^{-(-D_0)/kT} \cdot \frac{kT}{B_e} \cdot \frac{1}{1 - e^{-h\nu/kT}}$$

$q_{\text{rot}} q_{\text{spin}} = \sum (2J+1) e^{-B_e J(J+1)/kT}$   
 $\approx \int_0^{\infty} (2J+1) e^{-J(J+1) B_e/kT} dJ$   
 $\approx \frac{1}{2} \text{ or } \frac{kT}{B_e}$   
 Symmetry number  $\sigma = 2$   
 ground spin  
 comes in as  $\frac{1}{\sigma} (2I_A + 1)(2I_B + 1)$

These drop out from  $\frac{q_I}{q_{I_2}}$

$$B_e = \frac{h^2}{2I_e}$$

$\therefore q_{\text{rot}} = \frac{8\pi I_e kT}{h^2}$  (moment of inertia)

$$K_p = \frac{kT}{V} \cdot \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V \cdot 4 \right]^2$$

$$= \frac{kT \cdot \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \cdot 16 \cdot (1 - e^{-hv/kT})^2}{2^{3/2} e^{D_0/kT} \cdot 8\pi^2 I_0 kT}$$

$$= \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \cdot \frac{4}{\pi^2 I_0 h} \cdot \frac{(1 - e^{-hv/kT})}{e^{D_0/kT}}$$

$m = 127$  (or  $126.904$ )  $\text{amu} \times \frac{1 \text{ gram}}{6.022 \times 10^{23} \text{ amu}} = 2.11 \times 10^{-22}$

$I_0 = \text{given} = 750.2 \times 10^{-40} \text{ g cm}^2$

$v = \text{given} = 213.67 \text{ cm}^{-1}$   
 $300 \text{ K} = 2085 \text{ cm}^{-1} \rightarrow \frac{hv}{kT} = \frac{213.67 \times 300 \text{ K}}{208.5 \text{ T}}$

$D_0 = \text{given} = 35603 \text{ cal/mole}$   
 $1 \text{ cal/mole} = 0.349746 \text{ cm}^{-1} \rightarrow \frac{D_0}{kT} = \frac{35603 \times 0.349746}{208.5} \times \frac{300 \text{ K}}{\text{T}}$

$\left( \frac{\pi m kT}{h^2} \right)^{3/2} = \text{cm}^{-3}$  has units of  $\frac{1}{V}$

$$K_p = \frac{22.3 \text{ T}^{3/2} (1 - e^{-3074/T}) (e^{-17917/T}) \text{ atm}}{\left( \frac{2.257 \times 10^{-2} \text{ T}^{3/2} \text{ g cm}^{-3}}{4 (\pi m kT)^{3/2}} \right) \times \frac{82.05 \text{ cm}^3 \text{ atm mole}^{-1}}{8.3143 \times 10^7 \text{ erg K}^{-1}}} = 22.3 \text{ atm}$$

T	$K_p$ calc (atm)	$K_p$ observed (atm)
1073	$1.095 \times 10^{-2}$	$1.14 \times 10^{-2}$
1273	$1.68 \times 10^{-1}$	$1.65 \times 10^{-1}$
1473	1.24	1.23

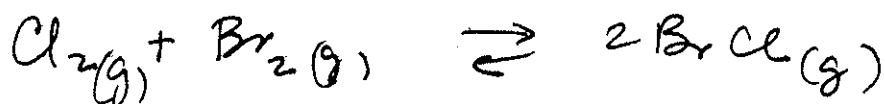
} QUITE GOOD!

9.  $\Delta G^\circ = -RT \ln K_p$

need to calculate  $K_p$  to find  $\Delta G^\circ$

Assume no vibrational excitation:

$q_{vib} = 1$        $q_{elec} = 1$  also



$K_p = \frac{q_{\text{BrCl}}^2}{q_{\text{Cl}_2} q_{\text{Br}_2}}$  in this case

$\sigma = 2$  for  $\text{Br}_2, \text{Cl}_2$   
 $\sigma = 1$  for  $\text{BrCl}$

$q = q_{\text{trans}} \cdot q_{\text{elec}} \cdot q_{\text{vib}} \cdot q_{\text{rot}} \cdot q_{\text{spin}}$

$q_{\text{BrCl}} = \left( \frac{2\pi(m_B + m_C)kT}{h^2} \right)^{3/2} \cdot V \cdot 1 \cdot 1 \cdot \frac{8\pi^2 I_0 kT}{h^2} \cdot \frac{1}{1}$

$\mu = \frac{m_B m_C}{m_B + m_C}$   
 $r = 1.14 + .99 \text{ \AA}$   
 $= 2.13 \text{ \AA}$

$q_{\text{Br}_2} = \left( \frac{2\pi(2m_B)kT}{h^2} \right)^{3/2} \cdot V \cdot 1 \cdot 1 \cdot \frac{8\pi^2 I_0 kT}{h^2} \cdot \frac{1}{2}$

$\mu = \frac{m_B}{2}$   
 $r = (1.14)^2$   
 $= 2.28 \text{ \AA}$

$q_{\text{Cl}_2} = \left( \frac{2\pi(2m_C)kT}{h^2} \right)^{3/2} \cdot V \cdot 1 \cdot 1 \cdot \frac{8\pi^2 I_0 kT}{h^2} \cdot \frac{1}{2}$

$\mu = \frac{m_C}{2}$   
 $r = (0.99)^2$   
 $= 1.98 \text{ \AA}$

$\Delta E_0 = -0.387 \text{ cal} \times 4974.6 \text{ cm}^{-1} = -135.35 \text{ cm}^{-1}$

9. cont'd

$$\Delta E_0/kT = \frac{-135.35}{208.5} \times \frac{300}{298} = -0.6535$$

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$$K_p = \frac{(m_B + m_C)^3}{(2m_B)^{3/2} (2m_C)^{3/2}} \frac{\left(\frac{m_B m_C}{m_B + m_C}\right)^2 (2.13)^4 e^{+0.6535}}{\left(\frac{m_B}{2}\right) (2.28)^2 \left(\frac{m_C}{2}\right) (1.48)^2 \frac{1}{2} \cdot \frac{1}{2}}$$

$$= \frac{(m_B + m_C)^2 (2.13)^4 e^{+0.6535}}{2 m_B^{1/2} m_C^{1/2} (2.28)^2 (1.48)^2} =$$

$$m_B = 74.909$$

$$m_C = 35.453$$

$$= \frac{4.3348 (1.00999) e^{+0.6535}}{1.922} = 8.417$$

$$\Delta G^0 = -RT \ln 8.417 = -1261 \text{ Cal}$$

$1.987 \text{ cal} \times 298 \text{ K}$   
 or  $592.13 \text{ cal}$

close to accepted value of -1211 cal