

Chemistry 448

Problem Set 4

$$\bar{E} = \frac{\sum_i \epsilon_i e^{-\epsilon_i/kT}}{\sum_i e^{-\epsilon_i/kT}}$$

$$\epsilon_i = (v + \frac{1}{2})h\nu \quad - (v + \frac{1}{2})h\nu/kT$$

In units of $h\nu$

$$\bar{E} = \frac{\sum_{v=0}^{\infty} (v + \frac{1}{2}) e^{-(v + \frac{1}{2})h\nu/kT}}{\sum_{v=0}^{\infty} e^{-(v + \frac{1}{2})h\nu/kT}} = \frac{1}{2} + \frac{e^{-\frac{h\nu}{2kT}} \sum_{v=0}^{\infty} v e^{-v h\nu/kT}}{e^{-\frac{h\nu}{2kT}} \sum_{v=0}^{\infty} e^{-v h\nu/kT}}$$

$$= \frac{1}{2} + \frac{\sum_{v=0}^{\infty} v e^{-v h\nu/kT}}{\sum_{v=0}^{\infty} e^{-v h\nu/kT}}$$

geometric series $\sum_{v=0}^{\infty} e^{-vu}$ is of the form

$$\sum_{n=0}^{\infty} x^n \quad \text{where } x \equiv e^{-u}$$

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \dots = \sum_{n=0}^{\infty} x^n$$

$$\therefore \sum_{v=0}^{\infty} e^{-vu} = \frac{1}{1 - e^{-u}}$$

geometric series $\sum_{v=0}^{\infty} v e^{-vu}$ is of the form

$$\begin{aligned} \sum_{n=0}^{\infty} n x^n &= 0 + x + 2x^2 + 3x^3 + \dots \\ &= [1 + 2x + 3x^2 + 4x^3 + \dots] - [1 + x + x^2 + x^3 + \dots] \\ &= \frac{1}{(1-x)^2} - \frac{1}{1-x} \end{aligned}$$

$$= \frac{1 - (1-x)}{(1-x)^2} = \frac{x}{(1-x)^2}$$

$$\therefore \sum_{v=0}^{\infty} v e^{-vu} = \frac{e^{-u}}{(1-e^{-u})^2}$$

$$\begin{aligned} \bar{E} &= \left\langle v + \frac{1}{2} \right\rangle^T = \frac{1}{2} + \frac{e^{-u}}{(1-e^{-u})^2} \cdot \frac{1}{1-e^{-u}} = \frac{1}{2} + \frac{e^{-u}}{1-e^{-u}} \\ &= \frac{\frac{1}{2}(1-e^{-u}) + e^{-u}}{1-e^{-u}} \\ &= \frac{1}{2} \frac{(1+e^{-u})}{(1-e^{-u})} = \frac{1}{2} \frac{e^{u/2} + e^{-u/2}}{e^{u/2} - e^{-u/2}} \\ &= \frac{1}{2} \coth\left(\frac{u}{2}\right) \end{aligned}$$

$$\left\langle v + \frac{1}{2} \right\rangle^T = \frac{1}{2} \coth\left(\frac{hv}{2kT}\right) \quad \text{Q.E.D}$$

If we use derived formulas:

$$\bar{E} = - \left(\frac{\partial \ln q}{\partial \beta} \right)$$

$$\text{and } q = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}$$

$$\text{Then } \ln q = -\beta h\nu/2 - \ln(1 - e^{-\beta h\nu})$$

$$- \frac{\partial \ln q}{\partial \beta} = -\frac{h\nu}{2} - \frac{+ h\nu e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}$$

$$\bar{E} = h\nu \left[\frac{1}{2} + \frac{e^{-\beta h\nu}}{1 - e^{-\beta h\nu}} \right] = h\nu \left[\frac{\frac{1}{2}(1 - e^{-\beta h\nu}) + e^{-\beta h\nu}}{1 - e^{-\beta h\nu}} \right]$$

$$= h\nu \left[\frac{\frac{1}{2} + \frac{1}{2}e^{-\beta h\nu}}{1 - e^{-\beta h\nu}} \right] \times \left(\frac{e^{+\beta h\nu/2}}{e^{+\beta h\nu/2}} \right) = h\nu \cdot \frac{1}{2} \left[\frac{e^{\beta h\nu/2} + e^{-\beta h\nu/2}}{e^{\beta h\nu/2} - e^{-\beta h\nu/2}} \right]$$

\bar{E} in units of $h\nu$

$$= \frac{1}{2} \coth\left(\frac{\beta h\nu}{2}\right) = \frac{1}{2} \coth\left(\frac{h\nu}{2kT}\right)$$

2. a) $C_V \equiv \left(\frac{\partial E}{\partial T}\right)_V$ (vibr. only) = $N \left(\frac{\partial \bar{E}_{vib}}{\partial T}\right)_V = N h\nu \frac{1}{2} \frac{\partial}{\partial T} \coth\left(\frac{h\nu}{2kT}\right)$

$$= \frac{1}{2} N h\nu \cdot \frac{h\nu}{2kT^2} \cdot \frac{4e^{h\nu/kT}}{[e^{h\nu/kT} - 1]^2}$$

$$= \frac{N(h\nu)^2}{kT^2} \frac{e^{h\nu/kT}}{[e^{h\nu/kT} - 1]^2}$$

$$\frac{C_V}{R} = \left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{[e^{h\nu/kT} - 1]^2}$$

$$e^u = 1 + u + \frac{u^2}{2!} + \frac{u^3}{3!} + \dots$$

as $u \rightarrow 0$ $e^u \rightarrow 1 + u + \frac{u^2}{2}$

$$\frac{C_V}{R} \rightarrow \frac{u^2 (1 + u + \frac{u^2}{2} + \dots)}{(u + \frac{u^2}{2} + \dots)^2} \rightarrow 1 \text{ high temperature limit}$$

As $T \rightarrow 0$ $e^{h\nu/kT} \gg 1$
neglect 1 relative to $e^{h\nu/kT}$

$$\frac{C_V}{R} = \left(\frac{h\nu}{kT}\right)^2 e^{-h\nu/kT} \rightarrow 0$$

or as $T \rightarrow 0$ only $v=0$ is populated,

$$E = N \frac{h\nu}{2} \text{ so } \left(\frac{\partial E}{\partial T}\right)_V \equiv 0$$

$$\frac{h\nu}{2k} \frac{1}{T} \frac{1}{2} \coth^2\left(\frac{h\nu}{2kT}\right)$$

$$\left[\frac{1}{2} \left(e^{\frac{h\nu}{2kT}} - e^{-\frac{h\nu}{2kT}} \right) \right]^2$$

$$\left[\frac{e^{h\nu/2kT}}{\frac{1}{2}(e^{h\nu/kT} - 1)} \right]^2$$

$$\frac{4e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

Therefore: $C_v \text{ total} = \frac{3}{2}R + R + R = \frac{7}{2}R$
 ($T \rightarrow \infty$) transl rot. vib

$C_v \text{ total} = \frac{3}{2}R + R + 0 = \frac{5}{2}R$
 ($T \rightarrow 0$)

At intermediate T $C_v \text{ total} = \frac{3}{2}R + R + R \left[\frac{u^2 e^u}{(e^u - 1)^2} \right]$

3. The vapor pressure depends on $S_{\text{vapor}} - S_{\text{cryst}}$ (for a solid) or $S_{\text{vapor}} - S_{\text{liq}}$ (for a liquid). [Clayton equation].

In the case of Thallium, as in crystals of elements, the coupling of electron spins between neighboring atoms means that in the crystal $g_{\text{elec}} = 1$. In the vapor however, since the ground state is $^2P_{1/2}$ for Tl atoms, $g_{\text{elec}} = 2$. The entropy difference therefore includes a non-cancelling electronic contribution even at temperatures in which only the lowest electronic state is populated.

4. $^{16}\text{O}_2$ molecule at 3000 K, $kT = 2085 \text{ cm}^{-1}$

electronic state	degeneracy	energy
$^3\Sigma_g^-$	3	0 cm^{-1}
$^1\Delta_g$	2	7918.1 cm^{-1}
$^1\Sigma_g^+$	1	13,195.2 cm^{-1}

$g_{\text{elec}} = (3 + 2 e^{-7918.1/2085} + 1 e^{-13,195.2/2085})$

$3 + 0.04485 + 0.001784 = 3.0466$

$A = -NkT(\ln \frac{q_{\text{vapor}}}{q_{\text{cryst}}} + 1) - NkT \ln q_{\text{int}}$

$A = -NkT \ln g_{\text{elec}} = -1.987 \times 3000 \ln 3.0466 \text{ cal/mol}$

(both electronic contribution) = 6.6407 kcal/mol

5. The correct behavior for C_v of H_2 gas is
 not I (does not have the correct weighting according to spin degeneracies of each J level)
 not IV (This is only good at the high temperature limit and in any case a symmetry number would have to be included if this is used) This is the dashed line at $\frac{5}{2}$

Curve III is correct only if a paramagnetic catalyst is present to allow $ortho \leftrightarrow para$ conversion continuously, add ortho and para separately, with fractions changing with temperature

Curve II is correct because it uses a fixed fraction $\frac{3}{4}$ for the ortho even in the $T=0$ limit. This would be observed if no $ortho \leftrightarrow para$ conversion is possible and the gas is prepared originally at high temperature ("normal" hydrogen) and then taken down in temperature.

$$6. \quad K_1 = \frac{[H^+][HA^-]}{[H_2A]} \quad K_2 = \frac{[H^+][A^-]}{[HA^-]} \quad \frac{K_1}{K_2} = \frac{[HA^-]^2}{[H_2A][A^-]}$$

If we assume that A^- and HA and H_2A have nearly the same structures then g_{trans} will be identical, so will g_{vib} , g_{elec} are all for ground state. g_{rot} will differ not much in the moment of inertia so only the symmetry numbers will be different: these are $\sigma = 1$ for HA , $\sigma = 2$ for H_2A and A^- . Therefore $\frac{K_1}{K_2} \approx \frac{(\frac{1}{\sigma})_{HA}^2}{(\frac{1}{\sigma})_{H_2A} (\frac{1}{\sigma})_{A^-}} = \frac{1^2}{\frac{1}{2} \cdot \frac{1}{2}} = 4$

Thus, the second ionization constant of symmetrical dibasic acids are $\leq \frac{1}{4} K_1$.

⑦ For a reaction $A + B \rightarrow AB$
 the entropy change at $T \rightarrow T_0$ is:

$$\Delta S_0 = k \ln t_{AB} - k \ln t_A - k \ln t_B$$

where t_A is the number of configurations of the reactant A, etc., in the limit of T_0 .

$$\Delta S_0 = k \ln \frac{t_{AB}}{t_A \cdot t_B}$$

In the perfectly ordered crystal the only degeneracy left is the degeneracy of the nuclear spins, $g_{\text{nucl}} = 2I + 1$ for each nucleus; $t_{AB} = [g_{\text{nucl}}^{\text{cryst}}(AB)]^N$, $t_A = [g_{\text{nucl}}^{\text{cryst}}(A)]^N$, $t_B = [g_{\text{nucl}}^{\text{cryst}}(B)]^N$
 Since there is no change in the identity of the

then all the $(2J+1)$ terms cancel

nuclei in a chemical reaction, then the ratio $t_{AB}/t_A \cdot t_B = 1$ so that $\Delta S_f = 0$. However, if there is some residual random arrangement of molecules in the crystal, t_A (for example) will be $[g_{\text{nucl}}(A) \cdot 2]^N$ if there are 2 ways of arranging (up or down) a diatomic molecule in the crystal.

Then for A, $s(A) = k \ln 2^N$, the same quantity by which the calorimetric entropy differs from the spectroscopic one. In general, for a reaction $aA + bB + \dots \rightarrow lL + mM + \dots$

$$\Delta S_0 = [l s(L) + m s(M) + \dots] - [a s(A) + b s(B) + \dots]$$

For $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$:

$s(\text{CO}) = k \ln 2^N$ (very small dipole moment of CO, crystal has randomly arranged up or down CO molecules. $s(\text{CO}_2) = 0$, $s(\text{O}_2) = 0$ (despite the fact that O_2 has a ground state triplet for which $g_{\text{elec}}^{\text{gas}} = 3$, in the crystal the electron spins of the neighboring molecules are coupled so in the crystal $g_{\text{elec}}(\text{O}_2) = 1$. Therefore for this reaction

$$\begin{aligned} \Delta S_0 &= 2s(\text{CO}_2) - 2s(\text{CO}) - s(\text{O}_2) = 0 - 2k \ln 2^N \\ &= -2R \ln 2 \end{aligned}$$

For $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$

$s(\text{Cl}_2) = 0$ $s(\text{HCl}) = 0$ (large dipole moment, all molecules lined up in the crystal). $s(\text{H}_2) = 0$ because $J=0$ level is nondegenerate, and even for ortho hydrogen the separation of the 3 components of the $J=1$

rotational levels is of the order of kT at 1.6 K; so that below 1 K therefore $g_{\text{ortho}}(\text{H}_2) = 1$. Thus, if ΔS_0 is obtained by extrapolation from measurements down to 1 K, $\Delta S_0 = 0$. On the other hand, if ΔS_0 is obtained by extrapolation from measurements above 10 K, for which $g_{\text{ortho}}(\text{H}_2) = 3$, $s(\text{H}_2) = \frac{1}{4} Nk \ln 1 + \frac{3}{4} Nk \ln 3$, in which case,

$$\Delta S_0 = 2s(\text{HCl}) - [s(\text{H}_2) + s(\text{Cl}_2)] = -\frac{3}{4} Nk \ln 3.$$

Aside:

Note that in class we talked about the additional entropy of H_2 (as an entropy of mixing) due to the existence of $\frac{1}{4}$ para + $\frac{3}{4}$ ortho states is 4.39 cal/deg-mole. This is different from $(\frac{3}{4} Nk \ln 3 + \frac{1}{4} Nk \ln 1)$ by $Nk \ln 4 = Nk \ln \underbrace{(2I+1)(2I+1)}_{\text{Fund}}$