Problem Set 4

Chemistry 448

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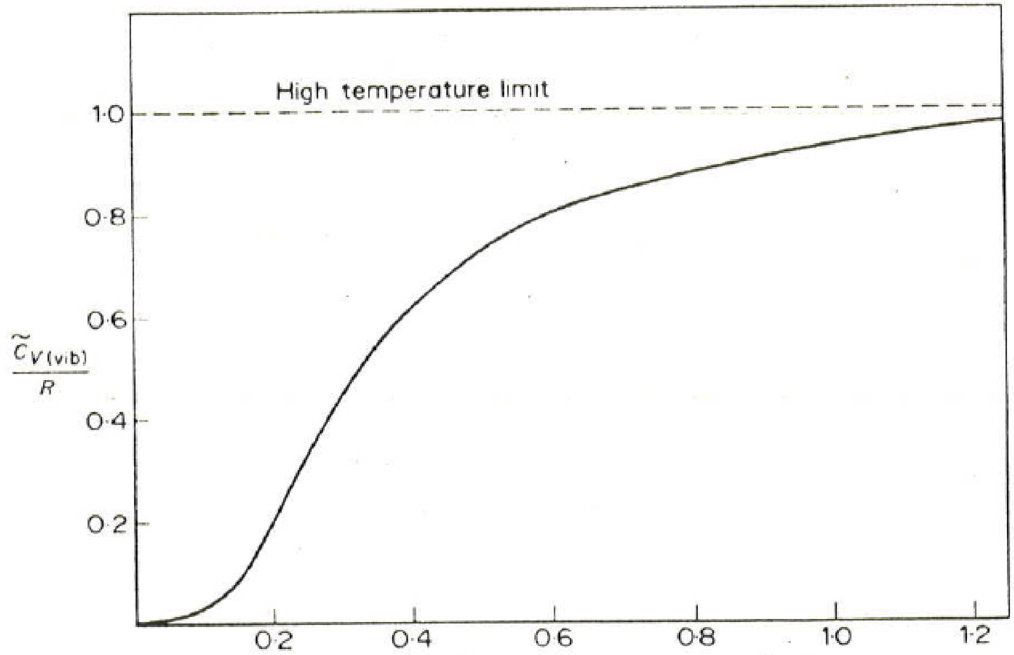
1. For a diatomic molecule, show that the average vibrational energy per molecule, $\bar{\varepsilon}_{vib}$ varies with temperature as follows:

$$\bar{\varepsilon}_{vib} = \langle v+½\rangle^{T} = ½\coth(h\nu/2kT)$$

2. The variation of the vibrational part of C_V with T/(hν/k) common to all diatomic gases is shown below:



(a) Show that this is indeed the case, that is, derive the equation for the curve shown and make sure that it goes to the indicated limits at low and high T/(hν/k).

(b) for T << hν/k $C_V = (5/2)R$
   for T >> hν/k $C_V = (7/2)R$
and for the intermediate temperatures

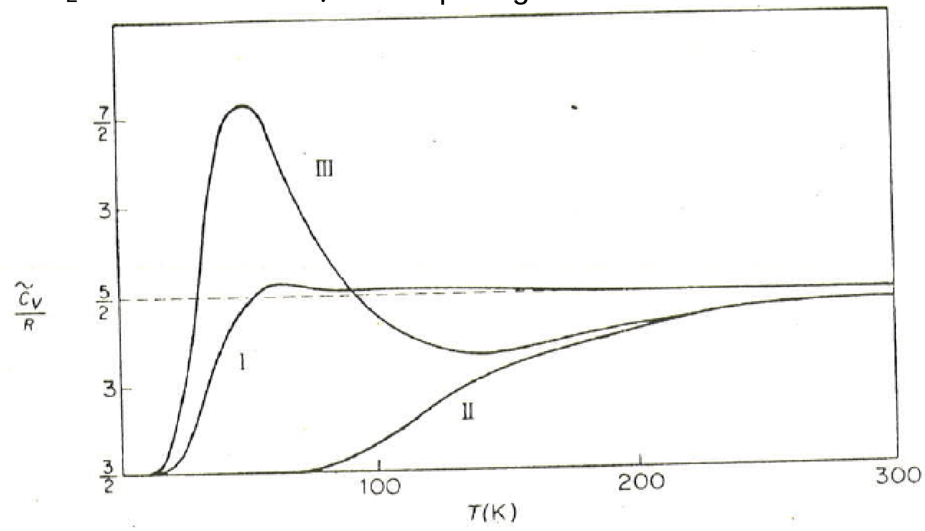
$$C_V = R\left[\frac{5}{2} + u^2 \frac{e^u}{(e^u - 1)^2}\right]$$

where u = hν/kT. Explain.

3. Explain why it is that the vapor pressure of thallium is partly determined by the fact that the lowest level of the Tl atom is $^{2}P_{1/2}$.

4. Consider the $^{16}O_2$ gas. For 3000 K calculate the contribution of the first two excited electronic levels (ground 0 cm^{-1}, 1st excited 7918.1 cm^{-1}, 2nd excited 13,195.2 cm^{-1}) to the Helmholtz free energy.

5. For H_2 the calculated C_V for the pure gas is shown below:



Curve I was calculated using $q_{rot} = \sum_{J=0}^{\infty}(2J+1)e^{-J(J+1)\hbar^2/8\pi^2 IkT}$

Curve IV was calculated using $q_{rot} = \frac{8\pi^2 IkT}{\hbar^2}$ not shown, <u>draw it in!</u>

Curve III was calculated using $\tilde{E} = x^{ortho}\tilde{E}^{ortho} + x^{para}\tilde{E}^{para}$

$$C_V = \left(\frac{\partial \tilde{E}}{\partial T}\right)_V = x^{ortho}\tilde{C}_V^{\ ortho} + x^{para}\tilde{C}_V^{\ para} + \left[\tilde{E}^{ortho}\left(\frac{\partial x^{ortho}}{\partial T}\right)_V + \tilde{E}^{para}\left(\frac{\partial x^{para}}{\partial T}\right)_V\right]$$

where $\tilde{C}_V^{ortho} = \left(\frac{\partial \tilde{E}^{ortho}}{\partial T}\right)_V$ and $\tilde{C}_V^{para} = \left(\frac{\partial \tilde{E}^{para}}{\partial T}\right)_V$

in which $x^{ortho} = \frac{n^{ortho}}{n^{ortho} + n^{para}} = \frac{\frac{n^{ortho}}{n^{para}}}{1 + \frac{n^{ortho}}{n^{para}}}$

$$\frac{n^{orhto}}{n^{para}} = \frac{3\sum_{J=1,3,5,\ldots}(2J+1)e^{-J(J+1)\Theta_{rot}/T}}{\sum_{J=0,2,4,\ldots}(2J+1)e^{-J(J+1)\Theta_{rot}/T}}, \text{ where } \Theta_{rot} = \frac{h^2}{8\pi^2 I}$$

whereas Curve II was calculated using $\tilde{C}_V = \frac{3}{4}\tilde{C}_V^{ortho} + \frac{1}{4}\tilde{C}_V^{para}$

Which is the correct (experimentally observed) behavior for C_V of this gas? Explain why the others are incorrect.

6. Let us represent a symmetrical dibasic acid [for example, adipic acid, $HOOC(CH_2)_4COOH$] as H_2A. Its ionization in water can be represented by the usual ionization equilibria:

$$H_2A = H^+ + [HA]^- \qquad K_1$$
$$[HA]^- = H^+ + A^= \qquad K_2$$

Knowing that equilibrium constants can be expressed in terms of molecular partition functions, explain why it is found that $(K_1/K_2) = 4$. That is, no experimental value of K_2 has ever been found to be greater than $\frac{1}{4}K_1$ for symmetrical dibasic acids. Explain/derive the ratio K_1/K_2.

7. We discussed several examples in which the entropy at temperature T_1 calculated from spectroscopic data, S_{spec}, differed from the entropy calculated from calorimetric data, S_{cal}, by a positive amount s, outside of experimental error:

$$S_{spec} = S_{cal} + s$$

We also discussed the two types of behavior leading to non-zero s as in (a) frozen-in randomness of orientation in the crystal, (b) wrong value of degeneracy assumed for temperature T_1 or 0 K, as in cases where ortho and para states exist.

Nernst's heat theorem, which you learned in freshman chemistry, states that for any process, $\Delta S_0 = 0$, where ΔS_0 is the entropy change associated with the reaction (for example, $A + B \rightarrow AB$) at T_0, a temperature sufficiently close to 0 K so that only a negligible fraction of the molecules are in levels other than ε_0 but not low enough for the splitting of the degenerate components of ε_0 to be important. If Nernst's heat theorem were true, it would be of great importance in chemistry because for a chemical reaction

$$aA + bB + \ldots \rightarrow lL + mM + \ldots$$

one could obtain

$$\Delta S = [\, lS_{cal}(L) + mS_{cal}(M) + \ldots \,] - [\, aS_{cal}(A) + bS_{cal}(B) + \ldots \,]$$

i.e., the entropy change of the chemical reaction at T_1 could be deduced entirely from the calorimetrically determined quantities S_{cal}. Unfortunately, this is not the case. While the above holds for some reactions, it does not hold for all.

(a) Derive ΔS_0 for a chemical reaction in terms of the number of configurations for each reactant and product.

(b) Under what conditions will ΔS_0 equal zero?

(c) For the reactions $2CO + O_2 \rightarrow 2CO_2$ and $H_2 + Cl_2 \rightarrow 2HCl$, ΔS_0 does not equal zero. What is ΔS_0 equal to in each case?