Chemistry 163C Midterm Spring 2013

Be sure to show all derivations and calculations,
and clearly mark your answers. Good Luck!

1) Consider a set of N distinguishable particles where each has a singly degenerate electronic ground state and a triply degenerate excited state of energy ε, as shown to the right. a) Write down the molecular partition function. b) Write down the canonical partition function. c) Evaluate q, the molecular partition function, at the limits $T \to 0$ and $T \to \infty$. d) Develop an expression for the internal energy U. e) Develop an expression for C_v and plot C_v vs T from zero to $T > \varepsilon/k$.

2) Consider a three level system of energies 0, ε, and 2ε.   The second level is doubly degenerate. a) Write down the molecular partition function. b) Develop an expression for the probability of occupying the middle level. c) Sketch this probability from $T = 0$ to $T \to \infty$. d) What value does the probability reach at $T \to \infty$? Briefly explain this result.

3) The dominant isotope of molecular oxygen ($^{16}O^{16}O$) is characterized by the spectroscopic constants $\tilde{v} = 1580$ cm^{-1} and $B = 1.45$ cm^{-1}. a) What is the rotational temperature for O_2? b) What is the vibrational temperature for O_2? c) At 300K, may we use the high temperature approximation for vibration and/or rotation? d) Write down the mathematical expression for the canonical partition function for O_2 taking into account translation, rotation and vibration.   e) At 300K, what is the probability for O_2 to simultaneously occupy the 1st excited vibrational state (n = 1) and the J = 5 rotational state?

4) The van der Waals (vdW) gas approximates a real gas by recognizing that molecules will fill space and also experience a pairwise attraction. The canonical partition function for a vdW gas is given by:

$$Q = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N (V-nb)^N \exp\left(\frac{\beta an^2}{V}\right)$$

where b corresponds to the molecular volume and a is a measure of the attractive force. a) Determine an expression for the internal energy U of a van der Waals gas. b) If a > 0, will the energy for a vdW gas be greater or less than an ideal gas? Briefly explain. c) For Ar, $a = 1.34$ L^2 atm/mol^2 and $b = 0.032$ L/mol. For a sample of Ar at 1.0 atm and 300K, what is the difference in U for an ideal vs vdW gas? (Hint: assume 1.0 L for volume and use the ideal gas law to determine the number of moles.) (Note: 1.0 L atm = 101.3 Joules.) d) Determine an expression for the constant volume heat capacity C_v for a vdW gas. Can you distinguish a vdW gas from an ideal gas by measurement of C_v?

1) a) $q = 1 + 3e^{-\beta\epsilon}$

$$-\;-\;-\;\uparrow\epsilon$$
$$=$$
$$-$$

b) $Q = (1 + 3e^{-\beta\epsilon})^N$

c) $q(T=0, \beta\to\infty) = 1$

$q(T\to\infty) = 4$

d) $U = -\dfrac{\partial}{\partial\beta}\ln(1 + 3e^{-\beta\epsilon})^N$

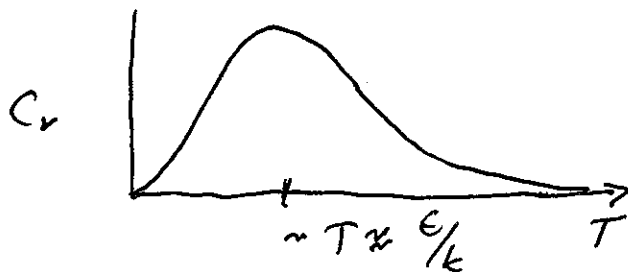$$= -N \frac{1}{1 + 3e^{-\beta\epsilon}} \cdot (-3\epsilon)e^{-\beta\epsilon}$$

$$= \frac{N\,3\,\epsilon}{e^{\beta\epsilon} + 3}$$

e) $C_v = -k\beta^2 \dfrac{\partial}{\partial\beta} \dfrac{N\,3\,\epsilon}{e^{\beta\epsilon} + 3}$
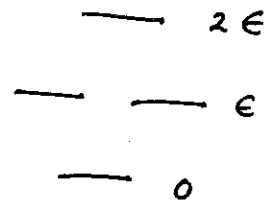
$$= +k\beta^2 \frac{N\,3\,\epsilon^2\,e^{+\beta\epsilon}}{(e^{\beta\epsilon} + 3)^2}$$

$$= \frac{N\,3\,(\beta\epsilon)^2\,e^{\beta\epsilon}}{(e^{\beta\epsilon} + 3)^2}$$
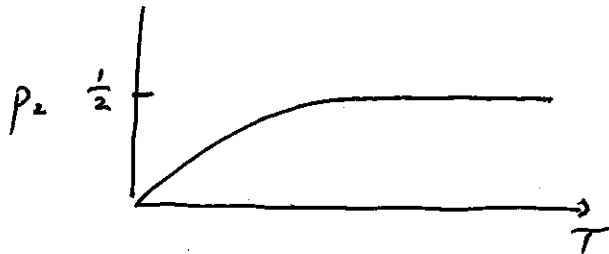
$C_v(T=0) = 0$; $C_v(T\to\infty) = 0$

C_v

$\sim T \asymp \epsilon/k$ T

2) a) $q = 1 + 2e^{-\beta\epsilon} + e^{-\beta 2\epsilon}$

$$\text{------} \quad 2\epsilon$$
$$\text{------} \;\; \text{------} \quad \epsilon$$
$$\text{------} \quad 0$$

b) $p_2 = \dfrac{2e^{-\beta\epsilon}}{1 + 2e^{-\beta\epsilon} + e^{-\beta 2\epsilon}}$

c) $p_2(T=0) = 0$; $p_2(T\to\infty) = \dfrac{2}{1+2+1} = \dfrac{1}{2}$

d) @ $T\to\infty$ $\beta\to 0$ $p_2 = \dfrac{1}{2}$

At inf. T, all states are equally populated. Two of four states are in level 2.

$$\therefore \quad \dfrac{2}{4} = \dfrac{1}{2}$$

3) $^{16}O_2$ $\quad \tilde{\nu} = 1580 \text{ cm}^{-1} \quad B = 1.45 \text{ cm}^{-1}$

a) $\Theta_R = \dfrac{hcB}{k} = 1.44 \dfrac{K}{cm^{-1}} \times 1.45 \text{ cm}^{-1}$

Note:
$\dfrac{hc}{k} = 1.44 \dfrac{K}{cm^{-1}}$

$\qquad = 2.09 \text{ K}$

b) $\Theta_V = \dfrac{hc\tilde{\nu}}{k} = 1.44 \times 1580 = 2275 \text{ K}$

c) high T approx is OK for rotation, <u>no</u>t vibration

d) $Q = \dfrac{1}{N!} \left(\dfrac{V}{\lambda^3} \cdot \dfrac{1}{\sigma \beta hc B} \cdot \dfrac{1}{1 - e^{-\beta hc\tilde{\nu}}} \right)^N$

e) $p(v, n=1) = (1 - e^{-\beta hc\tilde{\nu}}) e^{-\beta hc\tilde{\nu}} = 0.000508$

$p(R, J=5) = (2 \times 5 + 1) e^{-\beta hc B[5(5+1)]} (\beta hc B)$

$\qquad = (11)(0.812)(0.0070)$

$\qquad = 0.062$

$\therefore \text{ prob}(n=1, J=5) = 0.000508 \times 0.062$

$\qquad\qquad = 3.15 \times 10^{-5}$

4) $\quad Q = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N (V-nb)^N e^{\frac{\beta a n^2}{V}}$

a) $\quad U = -\frac{\partial}{\partial \beta} \ln\left[\frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N (V-nb)^N e^{\frac{\beta a n^2}{V}}\right]$

$\quad = -\frac{\partial}{\partial \beta}\left[\ln\frac{1}{N!} + \ln\left(\frac{V}{\Lambda^3}\right)^N + \ln(V-nb)^N + \beta\frac{a n^2}{V}\right]$

$\quad = -\frac{\partial}{\partial \beta}\left[N\ln\left(\frac{V}{\Lambda^3}\right) + \beta\frac{a n^2}{V}\right]$

$\quad U = \frac{3}{2}NkT - \frac{a n^2}{V}$

b) $\quad U(vdW) < U(ideal) \qquad$ molecules cluster lowering
$\qquad\qquad\qquad\qquad\qquad$ effective N

c) $\quad a = 1.34 \frac{L^2 atm}{mol^2} \qquad$ Ar $\quad 1.0\, atm \quad + 300\,k$

$\quad$ in $1.0 L \qquad n = \frac{(1.0L)(1.0\, atm)}{(0.0821\frac{L\cdot atm}{mol\cdot k})(300k)} = 0.0406\, mol$

$\quad U(ideal) - U(vdW) = \frac{a\cdot n^2}{V} = \frac{1.34 \times (0.0406)^2}{1.0}(101.3)$

$\qquad\qquad\qquad\qquad = 0.224\, J$

$\qquad$ Note: $U(ideal) = 151.6\, J \qquad \therefore$ small
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ correction

d) $\quad C_v = \left(\frac{\partial U}{\partial T}\right)_v$

$\quad = \frac{\partial}{\partial T}\left[\frac{3}{2}NkT - \frac{a n^2}{V}\right]$

$\quad = \frac{3}{2}Nk \qquad\qquad$ same as ideal gas

$\quad$ Cannot distinguish ideal vs vdW gas
$\qquad$ using C_v