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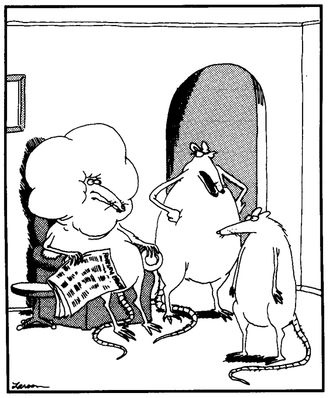
EXAM II

April 7, 2006



"Quit school? *Quit school?* You wanna end up like your father? A career lab rat?"

$k = 1.38 \times 10^{-23}\ \mathrm{J{\cdot}K^{-1}}$
$R = 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}} = 0.08314\ \mathrm{L\ bar\ K^{-1}\ mol^{-1}} = N_a k$

NAME: ____________________

TA: ____________________

This exam will be **closed book** and **closed notes**, but you will be permitted to use two 8.5" × 11" two-sided sheets of paper containing summary notes and equations.

Material covered
- Lectures 9-11, 13-16, 18-20
- Problem Sets 3-6

GRADING:
I. ____________ / 30
II. ____________ / 35 + 6 Extra Credit
III. ____________ / 35

TOTAL: ______ /100

Please show all of your work. When possible,
do not erase or cross out "false starts" on problems.

I. WATER IN THE SUN?

$\Delta G^\circ_{f,H_2O}(g, 298.15K) = -229 \text{ kJ mol}^{-1}$

$\Delta H^\circ_{f,H_2O}(g, 298.15K) = -242 \text{ kJ mol}^{-1}$

$\bar{S}^\circ_{H_2O}(g, 298.15K) = 189 \text{ J K}^{-1} \text{ mol}^{-1}$

$\bar{C}^\circ_{p,H_2O}(g, 298.15K) = 34 \text{ J K}^{-1} \text{ mol}^{-1} = 4.04R$

$\bar{S}^\circ_{H_2}(g, 298.15K) = 131 \text{ J K}^{-1} \text{ mol}^{-1}$

$\bar{C}^\circ_{p,H_2}(g, 298.15K) = 29 \text{ J K}^{-1} \text{ mol}^{-1} = 3.47R$

$\bar{S}^\circ_{O_2}(g, 298.15K) = 205 \text{ J K}^{-1} \text{ mol}^{-1}$

$\bar{C}^\circ_{p,O_2}(g, 298.15K) = 29 \text{ J K}^{-1} \text{ mol}^{-1} = 3.53R$

At $T > 10^4$K (results from Statistical Mechanics: "Equipartition")

$\bar{C}^\circ_{p,H_2O} = 7R$ (independent of T for $T > 10^4$K)

$\bar{C}^\circ_{p,O_2} = \bar{C}^\circ_{p,H_2} = 4.5R$ (independent of T for $T > 10^4$K)

A. (6 points) Compute K_p for the reaction at T = 298.15K:

$$H_2(g,298.15K) + \tfrac{1}{2}O_2(g,298.15K) = H_2O(g,298.15K)$$

B. (9 points) Starting with 1 mole **each** of $H_2(g)$, $O_2(g)$, **and** $H_2O(g)$ in a constant p reaction vessel at T = 298.15K and p = 1.00 bar, compute the equilibrium pressures of all three gases. [**HINT**: K_p is enormous, so you do not need a calculator to answer this question.]

C. (5 points) Making the completely unjustified assumption that $\Delta H^\circ_{f,H_2O}(g)$ and ΔS°_{rxn} are independent of T over the range T = 298.15K → T = 10^6K, compute K_p at T = 10^6K for the water formation reaction in part **A**.

D. (7 points) Now repeat the calculation of K_p at T = 10^6K using a more accurate scheme to take into account the T dependence of the thermodynamic quantities from which K_p is derived.

[**HINT**: you will need to account for the T-dependence of $\Delta H^\circ_{f,H_2O}(g)$ and ΔS°_{rxn}. It is a good approximation to ignore the T-dependence of $\Delta\bar{C}_p$ for the T range 298.15 K ≤ T < 10^4K where $\Delta\bar{C}_p$ is T-dependent and simply treat $\Delta\bar{C}_p$ as constant *at its high-T value* over the *entire* T range.]

* $\Delta\bar{C}_p(10^6\,K)$

* $\Delta H^\circ_{rx}(10^6\,K)$

* $\Delta S^\circ_{rx}(10^6\,K)$

* $K_p(10^6\,K)$

E. (3 points) Would you expect *any molecule* to be stable at T = 10^6K? Justify your answer.

Calculations for Question I

II. **STATISTICAL MECHANICS** [NO CALCULATOR NEEDED EXCEPT FOR **E**]

In this problem you will consider an idealized diatomic molecule that can rotate and vibrate, but for simplicity the molecule has only 4 energy levels. The 4 energy levels are labeled by the vibrational (v) and rotational (J) quantum numbers (v, J): (0,0), (0,1), (1,0), and (1,1).

$$\varepsilon_{v,J} = k[1000v + 10J]$$

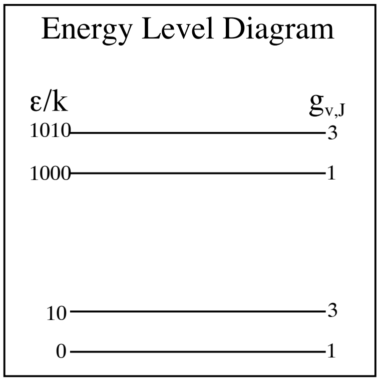
k is Boltzmann's constant and ε/k is in units of Kelvins. The energy levels have degeneracies given by $g_{v,J} = 2J + 1$. Thus the single molecule partition function and energy level diagram are:

$$q(T) = \sum_{v=0}^{1} \sum_{J=0}^{1} g_{v,J} e^{-\varepsilon_{v,J}/kT}$$

$$q(T) = \sum_{v=0}^{1} \sum_{J=0}^{1} (2J+1) e^{-(1000v+10J)/T}$$

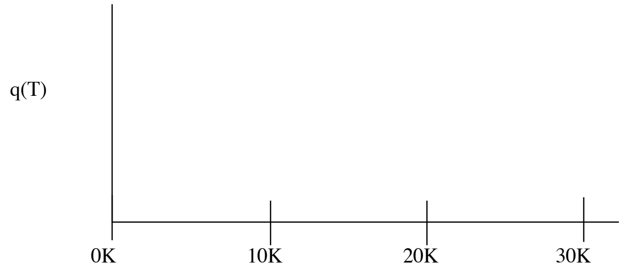
$$q(T) = \left(\sum_{v=0}^{1} e^{-1000v/T}\right)\left(\sum_{J=0}^{1}(2J+1)e^{-10J/T}\right) = q_{vib}q_{rot}$$

$$q(T) = \left(1 + e^{-1000/T}\right)\left(1 + 3e^{-10/T}\right)$$

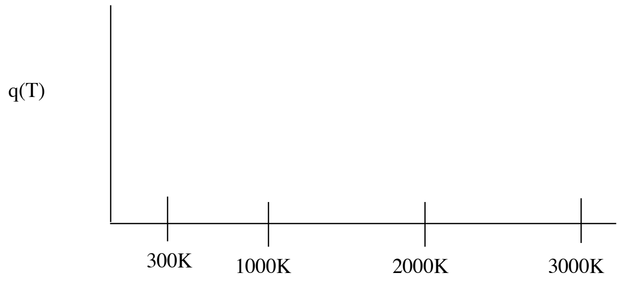


A (6 points) *Estimate* the value of q(T) at T = 0K, 100K, and 10,000K. [It would involve a prohibitive waste of time to actually attempt to compute q(T). Let $e^{-0.1} \approx 1, e^{-10} \approx 0$.]

B (4 points) Draw a rough sketch of q vs. T in the region 0K < T < 30K and another rough sketch of q(T) in the region 300K < T < 3000K.



0K < T < 30K



300K < T < 3000K

$\varepsilon_{v,J}/k = [1000v + 10J]$, $q(T) = (1+e^{-1000/T})(1+3e^{-10/T})$

C (6 points) Estimate the average value of the energy of one molecule at T = 0K, 100K, and 10,000K. [It is convenient to compute the average value of ε/k (units of Kelvins).]

D (6 points) Estimate the probability of finding the molecule in the v = 0, J = 1 level at T = 0K, 100K, and 10,000K?

E (4 points) At what finite T is the probability of finding the molecule in v = 0, J = 0 the same as in v = 1, J = 1?

$\varepsilon_{v,J}/k = [1000v + 10J]$, $q(T) = (1+e^{-1000/T})(1+3e^{-10/T})$

F (3 points) For a system of $N = 10^{23}$ indistinguishable molecules, express Q(T) in terms of q(T) at T = 0K, 100K, and 10,000K.

G (3 points) Use your answer to part **C** to determine a value for U/R (R is the gas constant, $R = N_a k$) for a system consisting of $N = 10^{23}$ indistinguishable molecules at T = 0K, 100K, and 10,000K.

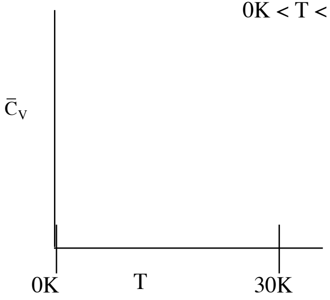
H (3 points) The following equation relates U to Q

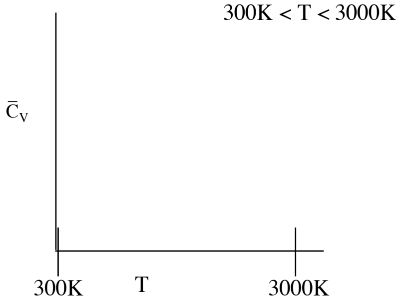
$$U = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}.$$

The value of Q depends on whether molecules are distinguishable or indistinguishable. Does the value of U depend on whether the particles are distinguishable? Why?

I (2 points) Sketch the rotation-vibration contribution to $\bar{C}_V$ over the $0K < T < 30K$ range and over the range $300K < T < 3{,}000K$. Identify the most important qualitative features in $\bar{C}_V$ vs. T. What does each feature tell you about $E_{v,J}$ and/or $g_{v,J}$?

Extra Credit





J (2 points) For a real diatomic molecule $E_{ROT} = BJ(J + 1)$ and $g_J = 2J + 1$, from which the rotational contribution to the molecular partition function

$$q_{ROT}(T) = \frac{kT}{B},$$

has been derived. B is the "rotational constant" (B is proportional to $1/r^2$ where r is the internuclear distance). Show that the rotational contribution to $\bar{C}_V$ is $R = N_ak$.

Extra Credit

K (2 points) The value of q(T) you estimated in part **A** stops increasing above some finite T, whereas the true $q_{ROT}(T)$ is proportional to T at all T (except at very low T). Why?

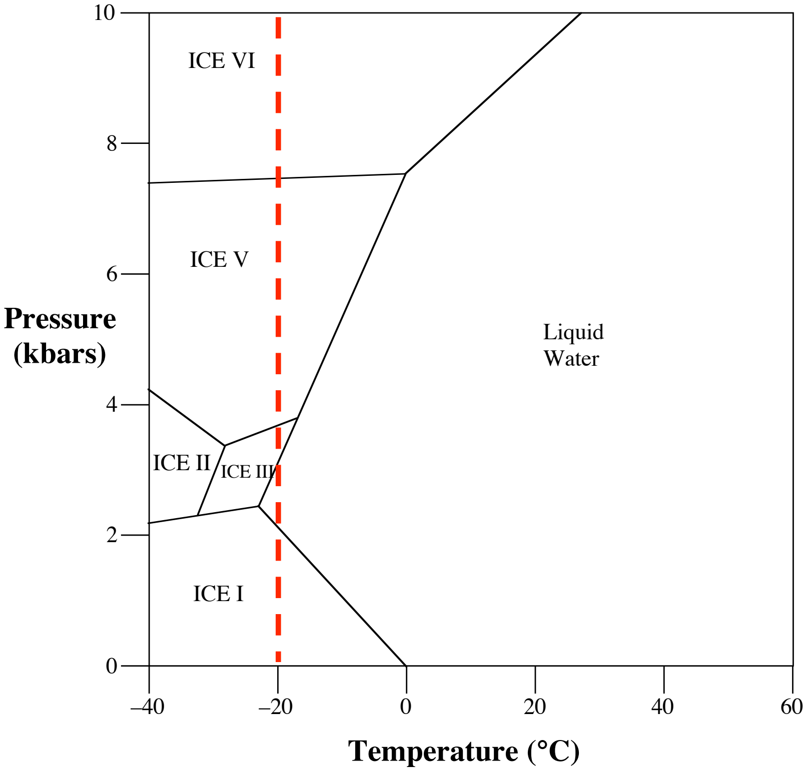
Extra Credit

Calculations for Question II

III. A VERY DIFFERENT KIND OF ICE SKATER: SLIDING GLACIERS?

You have seen many refutations, based on the Clausius-Clapeyron equation, of the specious claim that it is the pressure of an ice skater's sharp blade on the ice that causes some ice to melt even at $T < 0°C$, thus providing the lubrication that makes ice skating possible. But what about glaciers?

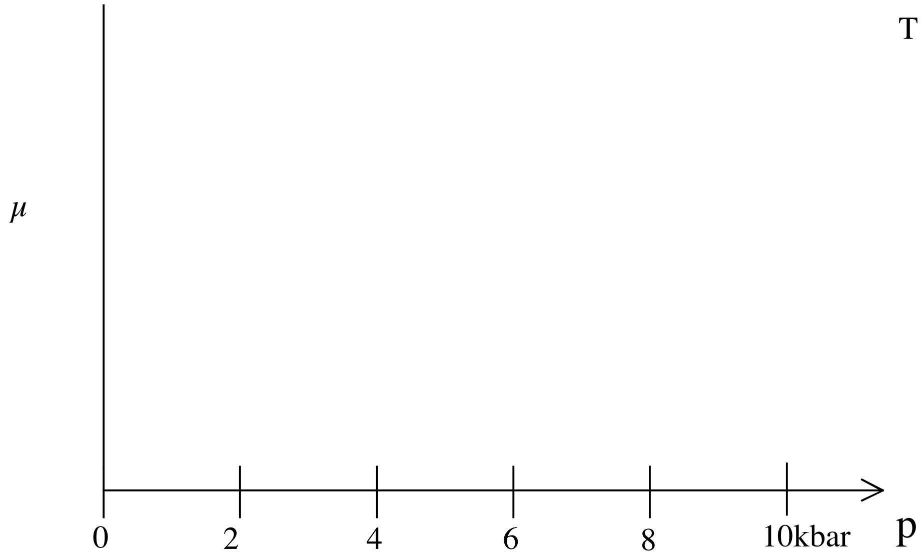
The phase diagram below displays the boundaries between liquid and solid phases of water.



A. (4 points) Within a single phase, does μ increase or decrease as p is increased at constant T? Why?

B. (8 points) Based on the information on the phase diagram, sketch μ vs. p at T = –20°C for 0 < p < 10kbar. Your sketch must show the *qualitative* behavior of $\mu(p,T)$ at constant T = –20°C for the most stable phase.

- What happens to μ and $\left(\frac{\partial \mu}{\partial p}\right)_T$ at each of the phase boundaries?
- Is there a discontinuity in μ or in $\left(\frac{\partial \mu}{\partial p}\right)_T$?
- If there is a discontinuity, to what measurable property is it related?



C. (4 points) The boundaries between Ice I and liquid and between Ice II and Ice V both have slopes opposite in sign from all other phase boundaries shown on the diagram. Discuss in terms of the Clapeyron equation [look at Part **D** for a useful hint].

D. (4 points) As pressure increases at constant T, $\bar{V}$ always decreases, even when crossing a phase boundary. As you cross from Ice II to Ice V does $\bar{S}$ increase or decrease? Why?
[**HINT**: what happens when you cross from Ice I to liquid water?]

E. (5 points) What is the pressure at the bottom of a 5 km thick glacier? Use
$\bar{V} = 1.8 \times 10^{-5}$ m^3 mol^{-1}, g = 9.81 m s^{-2}, 1Newton = 1 kg·m s^{-2},
1 N/m^2 = 10^{-5} bar.

F. (5 points) Liquid water at the bottom of a glacier might provide lubrication for the motion of the glacier over the non-smooth surface of the earth. If the temperature at the bottom of the glacier is T = –10°C, over what approximate range of glacier thickness will there be a liquid layer underneath the glacier? (If you *did not* obtain an answer to part **F**, use p = 1kbar at the bottom of a 5km thick glacier.)

G. (5 points) As global warming causes the average temperature of the earth's atmosphere to increase, some atmospheric models predict a significant increase in snowfall in the polar regions. The glaciers will get thicker. If the average T in the polar ice remains constant at around T = –10°C, what is likely to occur?

Calculations for Question III