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Physics 119A
Final Examination

Thursday 10 December, 2009

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QUESTION 1 (25 points)

TRUE or FALSE (if false, provide the correct answer/explain why it is false. If true, just write TRUE, you do not need to justify)

1. For a one component system: $\mu = \left(\frac{\partial H}{\partial n}\right)_{S,P}$

2. At the triple point $\mu_{solid} = \mu_{gas}$

3. Consider an ideal gas that is thermally isolated from the surroundings, and undergoes a free expansion to twice its initial volume. The temperature of the gas will increase.

4. ΔH_{mix} of two ideal gases is always positive.

5. For the isothermal reversible expansion of an ideal gas, ΔG is greater than ΔF.

6. For an monoatomic ideal gas, $\left(\frac{\partial C_v}{\partial V}\right)_T$ is always positive.

7. In a paramagnet system, negative temperatures are hotter than positive temperatures.

8. A paramagnetic sample in a magnetic field (B) is prepared so that 40% of the magnetic dipoles (μ) are in states which are anti-aligned with the direction of the magnetic. The temperature is positive.

9. The slope of the solid-liquid boundary line in the P-T phase diagrams is always positive.

Question 2: (25 points) <u>**Short Questions (There are 7 independent parts)**</u>

<u>Part 1:</u> We considered three model systems in this class: an ideal gas, an Einstein solid and a paramagnet. For each of theses systems, draw **qualitatively**:

a) a plot of S versus U

b) a plot of C_v versus T

Part 2: If an isolated Einstein solid is in thermodynamic equilibrium and has $N_A = 300$ oscillators in one subsystem and $N_{\boldsymbol{B}} = 200$ oscillators in the other subsystem, and if the entire solid has *100* units of energy, what is the most likely amount of energy to be observed in system B?

Part 3: The entropy S = S (N, U, A) of an ideal two-dimensional monoatomic gas consisting of N atoms, energy U , and area A is given by the following version of the Sackur-Tetrode equation:

$$S = Nk_B\left[2 + \ln\left(\left(\frac{2\pi m}{h^2}\right)\frac{A}{N}\frac{U}{N}\right)\right]$$

Here π is the two dimensional pressure (force per length as opposed to force per area).
Derive an expression for the pressure π of this two-dimensional gas (simplify your expression as much as possible).

<u>Part 4:</u> The vapor pressure P of solid ammonia in mm of Hg, in the vicinity of its triple point, is given by $\ln Ps = 23.03 - 3754/T$ and that of liquid ammonia by is given by $\ln Pl = 19.49 - 3063/T$. What are the latent heats of sublimation, vaporization and melting at or near the triple point?

<u>Part 5:</u> The energy of a photon gas is given by $U = \alpha V T^4$ and the entropy by $S(U,V) = \alpha U^{3/4} V^{1/4}$ where α is a constant. Find an expression for the **Gibbs Free Energy G** in terms of α, T and V.

Part 6: Use the appropriate Maxwell relation to show that: $\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$

Part 7: Consider one mole of a Van der Waals gas, with equation:

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2}$$

Consider a reversible adiabatic expansion from a volume V_1 to a volume V_2. Find an expression for the final temperature T_2 in terms of the initial temperature T_1, volume and other constants. You can consider Cv to be a constant.

Question 3: (15 points)

Calculate ΔS for the melting of 1 mol of H_2O (ice) at 5^oC and 1 bar (ie, solid to liquid transition). The molar heat capacity for liquid water is:

$$\overline{C_{P,l}} = 75 + 0.01T^2 \quad in \quad JK^{-1}mol^{-1}$$

The molar heat capacity for ice is:

$$\overline{C_{P,s}} = 37.3 \quad in \quad JK^{-1}mol^{-1}$$

The molar heat of melting at 0^oC and 1 bar is: 6.008 kJ/mol

Question 4: (20 points) There are 2 parts to this question

Consider 1 mol of a real gas obeying the following equation of state:

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{T\overline{V}^2}$$

with a=0.556 Pa m^6 mol^{-2} K
and b=64x10^{-6} m^3mol^{-1}

Part a) Consider the reversible isothermal change in state at 300K from an initial volume of 10 L to a final state of volume 20L. Calculate ΔS_{syst}

Part b) Consider the same change in state, but carried out irreversibly against an external pressure equal to the final pressure in part a. The surroundings are kept constant at T_{surr}=300K. Calculate ΔS_{tot}.

Question 5 (15 points):

Adsorption is the process of particles sticking to the surface of a solid (rather than getting absorbed inside of it). To model adsorption, consider a surface that consists of $M >> 1$ discrete sites; each site has two possible states: vacant (with energy $\varepsilon = 0$), or bound to a single atom (with energy εo). The system is held at constant temperature T. If $N >> 1$ atoms are bound (with $M >> N$), find expressions for the following parameters of the system of adsorbed atoms. (Take care to express each parameter in terms of the requested variables, and make simplifying approximations where appropriate).

(a) The energy, $U(N, \varepsilon o)$.

(b) The multiplicity, $\Omega(M, N)$.

c) The entropy, $S(M, N)$.

d) The Helmholtz free energy, $F(M, N, T, \varepsilon o)$.

f) Now, the system of adsorbed atoms is placed in thermal and diffusive contact with an ideal gas of the same type of atoms. In equilibrium, find the number of adsorbed atoms N as a function of the pressure P of the ideal gas (and other constants of the problem). Note that the chemical potential of an ideal gas is $\varepsilon = k_B T \ln\left(\frac{N}{\alpha V}\right)$ where α is a constant.

BONUS QUESTION

Consider a three-state paramagnetic material with N atoms. $N_{\uparrow}$ have spin up, $N_{\downarrow}$ have spin down and N_0 have spin component 0. Find an expression for the multiplicity.

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