Physical Chemistry Cumulative Exam Feb. 07, 2019

# DON'T PANIC

## Undergraduate Thermodynamics:

**1. a.** According to the equipartition theorem, internal energy per mole is ($U_m$ =) ? **(3 pts)**
**b.** What is a degree of freedom? **(3 pts)**
**c.** Can you describe a consequence of the equipartition theorem? (hint: what is the change of internal energy at constant temperature? Or maybe something about heat capacity?) **(3 pts)**

**2.** Is work an exact or inexact differential? Also, explain how reversible work and irreversible work are different. Let's use pressure-volume type work, for which $\partial w = -P_{ext}\,\partial V$. **(4 pts)**

**3.** For a process to be spontaneous, is it true that the change in Gibb's Energy must be negative (i.e. $\Delta G < 0$ J)? **(5pts)**

**4.** What are the three laws of thermodynamics? **(9 pts)**

**5.** Do you remember what Legendre Transforms are, and how they change the natural variables of a function?
**a.** The change in internal energy is: $\partial U = \left.\frac{\partial U}{\partial S}\right)_V \partial S + \left.\frac{\partial U}{\partial V}\right)_S \partial V = T\,\partial S - P\,\partial V$. as a result, what are the natural variables of U? **(1 pts)**
**b.** Enthalpy is defined as $H = U + PV$. What are the natural variables of H? Please prove your answer by determining the change in enthalpy, i.e. $\partial H$. **(3 pts)**
**c.** Likewise Helmholtz energy is $A = U - TS$. What are the natural variables of A? Please prove your answer. **(3 pts)**
**d.** Gibb's energy is $G = U - TS + PV$. What are the natural variables of G? Please prove your answer. **(3 pts)**

## Graduate Statistical Thermodynamics:

**6.** What is "statistical thermodynamics"? **(5 pts)**

**7. a.** If $\partial S = \frac{1}{T}\partial U + \frac{P}{T}\partial V$, what are the natural variables of entropy? **(2 pts)**
**b.** The canonical ensemble is based on a Legendre Transform on entropy: $S - \frac{U}{T}$. What are the natural variables of this function (and show your work!)? **(3 pts)**

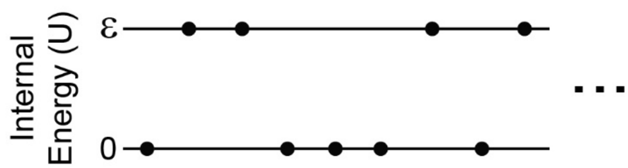
**8.** Statistical Mechanics generally uses one of three paradigms for analysis. Please provide a short description of: **(9 pts)**
**a.** The microcanonical ensemble.
**b.** The canonical ensemble.
**c.** The grand canonical ensemble.

**9.** The canonical partition function is:

$$Q = \sum_{\text{states}} e^{-U/k_B T}$$

we make the substation $\beta = \frac{1}{k_B T}$ to yield: $Q = \sum_{\text{states}} e^{-\beta U}$. Can you prove that $\langle U \rangle = \frac{-\partial \ln(Q)}{\partial \beta}$ ?
Hint: The probability (P) of a state having internal energy U is $P(U) = \frac{1}{Q} e^{-\beta U}$. **(10 pts)**

**10.** Let's examine a two-level system such as spins on a lattice like so:




These N number of particles (the little circles) do not interact with each other and can either have no energy (ground state) or ε energy (excited state).

**a.** Are these particles fermions or bosons, and why? **(2 pts)**
**b.** If the temperature is 0 K, all the particles are in the ground state. What is the entropy of that state? **(3 pts)**
**c.** Can you heat the system until all the particles are in the excited state? Hint: given $\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right)_V$, the temperature becomes very odd once the excited state population is over ½ full. **(4 pts)**
**d.** Calculate the single particle partition function:

$$q = \sum_{\text{states}} e^{-\beta U}$$

where U is the internal energy and $\beta = \frac{1}{k_B T}$. The only two states are the ground and excited states. **(5 pts)**
**e.** For non-interacting systems, the total partition function Q is equal to $q^N$, where N is the number of particles. Can you show that $\langle U \rangle = \frac{-\partial \ln(Q)}{\partial \beta} = \frac{N\varepsilon \cdot e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} = \frac{N\varepsilon}{1+e^{\beta\varepsilon}}$ ? **(10 pts)**

## Safety: **2 pts/each**

**11.** What is a Chemical Hygiene Plan?

**12.** What organization oversees lab safety in the state of Illinois?

**13.** You find a very old bottle of THF in your lab. What are the hazards, and can you test for those hazards; if so, how often?

**14.** Which of these acids is more concentrated and thus dangerous: hydrochloric acid or sulfuric acid?

**15.** On your honor, do you know where the nearest fire extinguisher and safety shower are in your work area(s)? **(yes or no only!)**

**General Equations:**

$\ln\left(\frac{a}{b}\right) = -\ln\left(\frac{b}{a}\right)$ $\ln(a^b) = b \cdot \ln(a)$ $\frac{\partial \ln(f(x))}{\partial x} = \frac{1}{f(x)} \frac{\partial f(x)}{\partial x}$

$C_p - C_v = n \cdot R$ $\left.\frac{\partial U}{\partial T}\right)_V = C_V$ $\left.\frac{\partial H}{\partial T}\right)_P = C_P$

$\partial U = \partial w + \partial q$ $\Delta w = -\int P_{ext}\, \partial V$ $\Delta w_{irrev} = -P_{ext}\Delta V$ $\Delta w_{rev} = -nRT \cdot \ln\left(\frac{V_f}{V_i}\right)$

$\partial U = \left.\frac{\partial U}{\partial S}\right)_V \partial S + \left.\frac{\partial U}{\partial V}\right)_S \partial V$ $\partial U = T\,\partial S - P\,\partial V$ $S = k_B \ln(W)$

Probability (P) of variable x: $\sum P(x) = 1.0$ Average value: $\langle f(x) \rangle = \sum f(x)P(x)$

Differential of a multi-variable function: $\partial f = \left.\frac{\partial f}{\partial x}\right)_y \partial x + \left.\frac{\partial f}{\partial y}\right)_x \partial y$

Legendre Transform: if $\partial f = C_x\, \partial x + C_y\, \partial y$ , then $g = f - C_y \cdot y$