Physical Chemistry Cumulative Exam
March 04, 2010
DON'T PANIC

General Thermodynamics:

1. a. What does the equipartition theorem state about a system's internal energy?
b. Can you describe one consequence of the equipartition theorem? (hint: you might want to think about heat capacities)

2. In general, we have four types of thermodynamic transitions, isothermal reversible, isothermal irreversible, adiabatic reversible, and adiabatic irreversible. Please write a 1 sentence description of each process.

3. If we define entropy as: $\partial S = \frac{\partial q_{rev}}{T}$, can adiabatic irreversible processes exist? If so, is this description of entropy fully correct?

4. We tell high school students that Gibb's energy must decrease for a process to be spontaneous ($\Delta G<0$). Now, when you got to college, we told you that total entropy must increase for a process to be spontaneous ($\Delta S_{tot}>0$). Why did we lie, or did we? Please resolve this issue.

5. If a chemical system produces heat ($\Delta H<0$) at constant temperature and constant pressure, is there a positive, negative, or no change in the surrounding's entropy? If the system entropy increases, what is the change in the total entropy? Now tell me whether Gibb's energy has increased or decreased.

6. If the Gibb's energy for a chemical process at constant temperature and constant volume is negative, is the process spontaneous? Explain your answer.

Statistical Mechanics:

7. In first year physical chemistry we cover four types of energy, Internal Energy (E), Enthalpy (H), Helmholtz Energy (A), and Gibb's Energy (G).
a. Why do we have four types of energy, given that the units of any one of these are in Joules?
(hint: I would be glad to accept any description of how one type of energy is different or unique compared to another ie. H vs. G)

8. The change in internal energy E for a given thermodynamic process is given by:
$\partial E = T\partial S - P\partial V + \mu\partial N$. Using the Euler's Theorem for 1^{st} order homogeneous equations, show me what the absolute internal energy is equal to. Show your work! Or I'll show you an F.

9. Why is the change in internal energy $\partial E = T\partial S - P\partial V + \mu\partial N$ a 1st order homogeneous equation? I'm just wondering how you answered #8 correctly...
(hint: tell me what a 1st order homogeneous equation is)

10. If entropy is "randomness," then we often use the mathematics of probability to analyze it. Turns out the result is: $S = -k_B \cdot \sum_i P_i \cdot \ln(P_i)$, where k_B is the Boltzmann constant, and P_i is the probability of observing outcome (or thermodynamic state) *i*. If we are examining several states of equal internal energy E, the probability P_i of any outcome (or state) is just 1/Ω where Ω is the total number of outcomes (or states). Show me that this is consistent with the Boltzmann formula $S = k_B \cdot \ln(\Omega)$

11. I can show that entropy is: $S = \frac{E}{T} + \frac{PV}{T} - \frac{\mu N}{T}$.

a. If you insert the equation $S = k_B \cdot \ln(\Omega)$ and subtract out the internal energy, can you put $S - \frac{E}{T}$ in the form of a natural log? hint: what your trying to do is show me that $S - \frac{E}{T} = \ln(?)$.

b. Now if you consider that the number of outcomes (or states) Ω is equal to the following summation: $\Omega = \sum_i states$, what does your answer to pt. a become? (hint: the answer to part a becomes the canonical partition function)

Safety:

12. a. What is a Chemical Hygiene Plan?
b. Do you know where your lab's chemical hygiene plan is? (yes or no only!)

13. What is a MSDS?

14. If an inspector comes into your laboratory, and there is a Coke can in the trash, do you get fined?

15. Is the energy of a laser or the power of a laser the determining factor in terms of whether you can be blinded by it?

16. Order these acids in terms of hazard: Nitric acid, sulfuric acid, hydrofluoric acid, hydrochloric acid, and explain why you ordered them as you did.

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

This is all you need.

Seriously, it is. Don't make things too hard.

Gas Constants	Atmospheric Pressures	
8.314 J / K / mol	101325 Pascals	
0.0821 atm L / K / mol	1.0 atm	
62.36 Torr L / K / mol	760 mmHg	T(°C) = T(K) -273.15
0.0831 bar L / K / mol	760 Torr	STP = 1 bar, 298.15K
1.206 psi L / K / mol	14.696 psi	
	1.01325 bar	

General Equations:

Euler's Theorem: If $\partial f(x,u) = \frac{\partial f}{\partial x}\cdot\partial x + \frac{\partial f}{\partial u}\cdot\partial u$ is 1st order homogeneous, then $f = \frac{\partial f}{\partial x}\cdot x + \frac{\partial f}{\partial u}\cdot u$

$\ln\left(\frac{a}{b}\right) = -\ln\left(\frac{b}{a}\right)$ $\quad \ln\left(a^b\right) = b\cdot\ln(a)$ If $\left(\frac{x}{y}\right)^z = \left(\frac{a}{b}\right)$ then $\left(\frac{y}{x}\right)^z = \left(\frac{b}{a}\right)$ and $\left(\frac{x}{y}\right) = \left(\frac{a}{b}\right)^{\frac{1}{z}}$

$\Delta U = \partial q + \partial w$; $\partial w = -\int_{V_i}^{V_f} P_{ext}\partial V$ Irreversible $\partial w = -P_{ext}\cdot\Delta V$ Reversible: $\partial w = -nRT\ln\left(\frac{V_2}{V_1}\right)$

$\partial E = \left(\frac{\partial E}{\partial S}\right)_V \partial S + \left(\frac{\partial E}{\partial V}\right)_S \partial V = T\partial S - P\partial V$ $\quad \partial q = n\cdot C_{p\ or\ v,m}\cdot\delta T$ $\quad \partial S = \frac{\partial q_{rev}}{T}$

$\Delta S = nR\ln\left(\frac{V_f}{V_i}\right) + nC_{p\_or\_v,m}\ln\left(\frac{T_f}{T_i}\right)$ $\quad \partial S \geq \frac{\partial q}{T}$ $\quad \left.\frac{\partial E}{\partial T}\right|_V = C_v$ $\quad \left.\frac{\partial H}{\partial T}\right|_P = C_p$ $\quad C_p - C_v = n\cdot R$

$\Delta H = \Delta E + \Delta(P\cdot V)$ $\quad$ If $\left.\frac{\partial x}{\partial y}\right)_z = \left.\frac{\partial a}{\partial b}\right)_c$ then $\left.\frac{\partial y}{\partial x}\right)_z = \left.\frac{\partial b}{\partial a}\right)_c$ $\quad \sum_i P_i = 1.0$

$\partial E = T\partial S - P\partial V$ $\quad \partial H = T\partial S + V\partial P$ $\quad \partial A = -S\partial T - P\partial V$ $\quad \partial G = -S\partial T + V\partial P$

Adiabatic Reversible Compression or Expansion.

$\left(\frac{T_f}{T_i}\right)^{\frac{C_v}{nR}} = \left(\frac{V_i}{V_f}\right)$; $\left(\frac{T_f}{T_i}\right) = \left(\frac{V_i}{V_f}\right)^{\frac{nR}{C_v}}$; $\left(\frac{P_i}{P_f}\right) = \left(\frac{V_f}{V_i}\right)^{\frac{C_p}{C_v}}$; $\left(\frac{P_i}{P_f}\right) = \left(\frac{T_i}{T_f}\right)^{\frac{C_p}{n\cdot R}}$ $\quad \partial w = n\cdot C_{v,m}\,\Delta T$

Partial Derivative Equations

$\partial f = \left(\frac{\partial f}{\partial x}\right)_y \partial x + \left(\frac{\partial f}{\partial y}\right)_x \partial y$ $\quad$ Euler Criterion: $\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y$

Legendre Transform $G(x,z) = F(x,y) - z\cdot y$ where $\left(\frac{\partial F}{\partial y}\right)_x = z$