Problem Set PS11

ISSUED: 11/16/00 **Due: 11/30/00**

Prof. Darin J. Ulness Name ______________________________

Instructions. Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

Mathematical Exercises

1. Solve the differential equation
$$\frac{dy}{dx} = \frac{x}{y}$$
by collecting all the x terms on one side of the equation and all the y terms on the other side of the equation and integrating each side of the resulting equation with respect to the appropriate variable.

2. Solve the differential equation
$$\frac{dy}{dx} = \frac{y}{x}$$
by the same method as in 1.

3. Solve the differential equation
$$\frac{d(\ln y)}{d(1/x)} = A,$$
where A is a constant, by the same method as in 1.

Exercises

4. Show that for a reversible process at constant pressure $\triangle H = q$ as we are taught in Freshman Chemistry.

5. Show
$$C_p = \left(\frac{\partial H}{\partial T}\right)_P.$$
You will want to consider dH for a reversible process at constant pressure and identify TdS as heat q.

6. Show the coefficient of thermal expansion,
$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P,$$
for an ideal gas is $\alpha = 1/T$. What does this say about how a gas behaves as one heats it?

7. Show that the isothermal compressibility,

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T,$$

for an ideal gas is $\kappa_T = 1/P$. What does this say about how a gas behaves under pressure?

8. Visit Stephanie Collins' legacy project on Joule-Thomson expansion (Fall 1998). Use what you learn there to show that the Joule-Thomson coefficient is zero for an ideal gas. Note unfortunately the Joule-Thomson coefficient is given the symbol μ which we will also use as the symbol for chemical potential.

9. Start with a blank sheet of paper and derive every equation in the on page 112 of the notes. Notice that the first working equation is our useful relation.

10. Thinking back to statistical mechanics, start with the partition function for the harmonic oscillator and derive the heat capacity (C_V) for an ensemble of harmonic oscillators. Plot C_V as a function of temperature. What happens to the heat capacity as $T \to 0$? In the limit of low T, how well does the heat capacity follow Debye's law?

11. Express the working equation for the internal energy of a Berthelot gas.

12. Derive K_a for the reaction $A + 2B \rightleftharpoons C$ by starting with the condition for equilibrium involving the chemical potentials of the reactants and products.

Conceptual Problems

13. Julie and Bor Yu are arguing over wether to use Helmholtz free energy (Julie) or Gibbs free energy (Bor Yu) to best describe a particular system. What information would you want regarding the system in order to decide who has the best approach to the problem. Under what conditions would it not matter which free energy is used?

14. Consider a mixture of gas A and gas B where the molecules of both gas A and Gas B tend to attract themselves whereas the dominant interaction between different types of molecules is repulsion. If gas A and gas B are in a container which for time $t < 0$ there is a wall separating the two gases, then at time $t = 0$ the wall is removed; what is the final state of the system at time $t \gg 0$ if

    (a) the minimization of total energy was the sole determinant of a spontaneous change?

    (b) the maximization of entropy was the sole determinant of a spontaneous change?

    Describe what you would really expect the final state of the gas to be.

15. Give "word" definitions of internal energy, enthalpy, free energy and chemical potential.

16. For each of the following state whether the relevant chemical potential which are listed in parentheses is positive or negative.

    (a) Ice at room temperature: (μ_{ice}).

    (b) Water on the side of a glass of ice cold lemonade on a hot humid summer day: (μ_{water}).

    (c) Helium inside a balloon (μ_{He}).

    (d) An iron bar outdoors (μ_{Fe})

17. Let's say the reaction $A \rightleftharpoons B$ has a $K_a = 2$. Sketch a graph of the chemical potential of the reactant A versus the reaction coordinate from pure A to pure B. Be sure to place the minimum of your curve at the appropriate mole fraction (assume the activity coefficients are always one).

18. Describe activity in your own words.

19. Discuss the idea of reference states in your own words.

20. Why can't we use all $\mu = 0$ as the equilibrium condition rather than saying all μ's are equal.

① $\frac{dy}{dx} = \frac{x}{y} \Rightarrow \int y\,dy = x\,dx$ $\boxed{\frac{y^2}{2} = \frac{x^2}{2} + C}$

② $\frac{dy}{dx} = \frac{y}{x} \Rightarrow \int \frac{dy}{y} = \frac{dx}{x}$ $\boxed{\ln y = \ln x + C}$

③ $\frac{d(\ln y)}{d(1/x)} = A \Rightarrow \int d(\ln y) = A\,d(1/x)$ $\boxed{\ln y = \frac{A}{x} + C}$

④ $dH = dU + P\,dV = dq - P_{ex}\,dV + P\,dV + V\,dP$

$P = P_{ex}$ reversible

$dH = dq - P\,dV + P\,dV + V\,dP$ → const P

$dH = dq \Rightarrow \Delta H = q$

⑤ reversible and const P

$dH = dq$ from #4

$\left(\frac{dH}{dT}\right)_P = \left(\frac{dq}{dT}\right)_P = C_P$ ✓

⑥ $V = \frac{nRT}{P}$ $\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$ so $\alpha = \frac{1}{V}\frac{nR}{P}$

$\alpha = \frac{P}{nRT}\frac{nR}{P} = \frac{1}{T}$ ✓

$\alpha > 0$ so an ideal gas expands when heated
the expansion is most pronounce at low T

⑦ $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ $\left(\frac{\partial V}{\partial P}\right)_T = -\frac{nRT}{P^2}$ so $\kappa_T = \frac{1}{V}\frac{nRT}{P^2}$

$\kappa_T = \frac{P}{nRT}\frac{nRT}{P^2} = \frac{1}{P}$

$\kappa_T > 0$ so an ideal gas shrinks as one applies pressure.

⑧ $\mu_{JT} = \frac{\left(T\frac{\partial V}{\partial T} - V\right)}{C_P}$ $V = \frac{nRT}{P}$ $\frac{\partial V}{\partial T} = \frac{nR}{P}$

$= \frac{\left(T\frac{nR}{P} - \frac{nRT}{P}\right)^0}{C_P} = 0$ ✓

⑨ Maxwell relations and working eqns

⑩ In[6]:= q = 1 / (2 Sinh[B h w / 2])

Out[6]= $\frac{1}{2}\text{Csch}\left[\frac{B h w}{2}\right]$

In[7]:= U = -1 / q D[q, B]

Out[7]= $\frac{1}{2} h w \,\text{Coth}\left[\frac{B h w}{2}\right]$

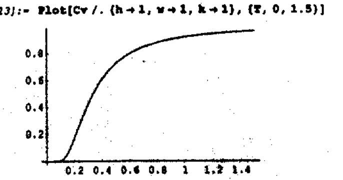
In[8]:= B = 1 / (k T)

Out[8]= $\frac{1}{k T}$

In[9]:= Cv = D[U, T]

Out[9]= $\frac{h^2 w^2 \,\text{Csch}\left[\frac{h w}{2 k T}\right]^2}{4 k T^2}$

In[13]:= Plot[Cv /. {h→1, w→1, k→1}, {T, 0, 1.5}]



Out[13]= - Graphics -

⑪ $dU = c_V\,dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV$ $P = \frac{nRT}{V-nb} - \frac{n^2a}{TV^2}$

$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb} + \frac{n^2a}{T^2V^2} \Rightarrow dU = c_V\,dT + \left[T\left(\frac{nR}{V-nb} + \frac{n^2a}{T^2V^2}\right) - \frac{nRT}{V-nb} + \frac{n^2a}{TV^2}\right]$

$\boxed{dU = c_V\,dT + \frac{2n^2a}{TV}dV}$

⑫ $A + 2B \rightleftharpoons C$

$\mu_A + 2\mu_B = \mu_C$ $\mu_i = \mu_i^\ominus + RT\ln a_i$

$\mu_A^\ominus + RT\ln a_A + 2\mu_B^\ominus + 2RT\ln a_B = \mu_C^\ominus + RT\ln a_C$

$\underbrace{\mu_A^\ominus + 2\mu_B^\ominus + \mu_C^\ominus}_{-\Delta_{rxn}G} = -RT\ln a_A - 2RT\ln a_B + RT\ln a_C$

$= RT\ln \underbrace{\frac{a_C}{a_A a_B^2}}_{Ka}$ $-\Delta_{rxn}G = -RT\ln Ka$

⑬ Conditions: const P or V const T etc.

If no PV work was done then it would not matter.

⑭ ⓐ [A | B] ⓑ [A B A B]

would expect some "clumpiness"

⑮ internal energy: total energy

enthalpy: total energy minus pV work energy

free energy: energy available to do work

chemical potential: potential to change the amount of material

⑯ ⓐ spontaneously ice will disapper

$dG = \mu\,dn$ so $\mu_{ice} > 0$

ⓑ spontaneously water will accumulate

$dG = \mu\,dn$ so $\mu_{H_2O} < 0$

ⓒ spontaneously He will leave the balloon

$dG = \mu\,dn$ so $\mu_{He} > 0$

ⓓ spontaneously Fe will goto Fe_2O_3

$dG = \mu\,dn$ so $\mu_{Fe} > 0$

⑰ skip

⑱⑲ your words

⑳ dynamic equilibrium must be able to change material