PHY 410 – Spring 2008 Exam #2

(1 Hour)

PLEASE WAIT UNTIL YOU ARE TOLD TO BEGIN THE EXAM

While waiting, carefully fill in the information requested below

Your Name:…………………………………………………………………

Your Student Number:…………………………………………………

There are 4 problems. Please answer them all.

USEFUL CONSTANTS AND EQUATIONS

Avogadro's Number N_A= 6.022 x 10^{23}
Boltzmann's constant k = 1.381 x 10^{-23} J/K
= 8.617 x 10^{-5} eV/K
Gas constant R = kN_A = 8.31 J/mol.K
Planck constant h = 6.626 x 10^{-34} J.s
Electron charge (magnitude) e = 1.602 x 10^{-19} C
Electron mass m = 9.109 x 10^{-31} kg

1 atm = 1.013 bar
1 bar = 10^5 N/m^2
1 eV = 1.602 x 10^{-19} J

Stirling's formula: ln x! ~ x lnx – x when x >> 1
Secur Tetrode equation for **3dimensional** gas

$$S(N,V,U) = kN\left[\ln\left\{\left(\frac{V}{N}\right)c\left(\frac{U}{N}\right)^{3/2}\right\} + \frac{5}{2}\right];\ c = \left(\frac{4\pi m}{3h^2}\right)^{3/2}$$

Problem 1 (10 points)

1 kg of ice at 0^oC is left sitting on a kitchen table, the temperature of the kitchen is 30^oC. Ice melts and then the water warms up to the kitchen temperature. Ignore any effect of the volume change. For: ice Latent heat of melting 333 J/g; For water : C_v= 4.186 J/gK.

i) Calculate the total change in the entropy of the water.(3 points)
ii) Calculate the change in the entropy of the bath (kitchen)as it gives up heat to first melt then to heat the water to 30^oC.(5 points)
iii) Is the net change in the entropy (ice+water and kitchen) positive or negative?(2)

(i) *For the ice water system*

$$\Delta S_{ice} = \frac{Q_{latent}}{T} = \frac{333\,kJ}{273K} = +1.220\ kJ/K$$

$$\Delta S_{water} = \int_{T_i}^{T_f} (C/T)dT = C\ln\frac{T_f}{T_i} = 4.186\,(kJ/K)\ln\frac{303K}{273K} = +0.436\,kJ/K$$

$$\Delta S_{tot,ice+water} = (1.220 + 0.436)\ kJ/k = +1.656\ kJ/K$$

(ii) *For the kitchen bath* (*which is at constant temperature* $303K$)

$$\Delta S_{tot,kitchen} = -\frac{333\,kJ + 4.186\,x\,30\,kJ}{303\,K} = -1.513\ kJ/K$$

(iii) *Total entropy change*

$$\Delta S_{net} = \Delta S_{tot,ice+water} + \Delta S_{tot,kitchen} = (+1.656 - 1.513)\ kJ/k = +0.143\ kJ/K$$

Total entropy must increase

Problem 2 (15 points)

The entropy of an ideal gas consisting of N particles confined to move in a one dimensional box of length L and total energy U is given by (c is a constant depending on mass, Planck's constant etc)

$$S(N,\ L,\ U) = Nk\left[\ln\left\{\left[\left(\frac{L}{N}\right)c\left(\frac{U}{N}\right)^{1/2}\right]\right\} + \frac{3}{2}\right]$$

Since S is given as a function of N, L, U, we use the **thermodynamic identity for entropy**:

$$TdS = dU + FdL - \mu dN \text{ since the work done is } -FdL\text{, where } F \text{ is the tension (sorry for the notation)}$$

(i) What is the temperature of this system? How does it depend on N, U, and L? (5 points)

$$\frac{1}{T} = (\partial S/\partial U)_{L,N} = \frac{\partial}{\partial U}\left[Nk\left\{\ln U^{1/2} + C(\text{independent of } U)\right\}\right] = (1/2)Nk/U$$

$$T = \frac{2U}{Nk};\ \propto U;\propto \frac{1}{N};\text{independent of } L$$

(ii) What is the equation of state for this system (corresponding to PV=NkT for an ideal three dimensional gas). Hint: The mechanical work done in one dimensional gas is FL where F is the tension (Force) along the gas which is the equivalent of P (Force/area) in three dimension?(5 points)

Use

$$TdS = dU + FdL - \mu dN$$

$$F = T(\partial S/\partial L)_{N,U}$$

$$= T\frac{\partial}{\partial L}\left[Nk\ln L + C(\text{independent of } L)\right]$$

$$= TNk/L$$

$$FL = NkT \text{ is the equation of state (corresponding to } PV = NkT \text{ for a 3d gas)}$$

Note that the dimension of energy is FL (Force x distance)

(iii) What is the temperature and density dependence of the chemical potential μ for this system? (5 points)

$$\mu = -T(\partial S / \partial N)_{U,L}$$

$$= -T\left[k \ln\left[\left\{ \frac{L}{N} c \left(\frac{U}{N} \right)^{1/2} \right\} + \frac{3}{2} \right] + Nk \frac{\partial}{\partial N} \left\{ \ln\left(\frac{1}{N^{3/2}} \right) + C \right\} \right]$$

$$= -T\left[k \ln\left[\left\{ \frac{L}{N} c \left(\frac{U}{N} \right)^{1/2} \right\} + \frac{3}{2} \right] - \frac{3}{2} \right]$$

$$= -kT \ln\left\{ \frac{L}{N} c \left(\frac{U}{N} \right)^{1/2} \right\} = -kT \ln\left\{ \frac{L}{N} c \left(\frac{kT}{2} \right)^{1/2} \right\}$$

$$\mu \propto \ln\left(\frac{1}{\rho} \right); \ \rho = N / L \ (density)$$

$$\mu \propto T \ln T^{1/2}$$

Problem 3 (15 points)

(i) Derive the "thermodynamic identity for the Gibb's free energy G". What are the natural thermodynamic variables (which control in a measurement) of G?
(5 points)

$$G = U - TS + PV$$
$$dG = dU - TdS - SdT + PdV + VdP$$
$$Use: dU = TdS - PdV + \mu dN$$
$$dG = -SdT + VdP + \mu dN$$
$$The\ natural\ thermodynamic\ variables\ of\ G\ are\ N, P, T$$

(ii) Using (i) obtain expressions for the entropy (S) and volume (V) in terms of partial derivatives of G.(2 points)

$$S = -(\partial G / \partial T)_{N,P}$$
$$V = (\partial G / \partial P)_{N,T}$$

(iii) For 1 mole of liquid water at 25°C and at 1 bar pressure, V=18.068 cm^3, and the coefficient of thermal expansion $\beta = (1/V)\left(\partial V/\partial T\right)_{P,N}$ = 2.57 x 10^{-4} 1/K.

a) What is the change in G if the pressure is increased to 11 bars.(3 points)

$$\Delta G = V\Delta P\ for\ constant\ T\ and\ N$$
$$= 18.068 x 10^{-6} m^3 x 10 x 10^5 N/m^2$$
$$= 18.068\ J$$

b) How much is the change in entropy for the same increase in pressure? (5 points)

For this we need to know how entropy S changes with pressure P at constant temperature T − N is fixed; $(\partial S / \partial P)_{N,T}$

We need Maxwell Relation: From (ii) $(\partial S / \partial P)_{N,T} = -(\partial V / \partial T)_{N,P} = -V\beta$

$$\Delta S = -V\beta\,\Delta P = -\beta \Delta G = -18.068 x 10^{-6} m^3 x\, 2.57 x 10^{-4} (1/K) x 10 x 10^5 (N/m^2)$$
$$= -4.643 x 10^{-3}\ J/K$$

Problem 4 (10 points)

a) A heat engine is used to extract useful work. It operates between 800^{o}C and 100^{o}C. What is the maximum amount of kilowatt-hours of energy that can be extracted for every kilowatt-hour of thermal energy extracted from the hot source?(4)

$$Efficiency\ \eta = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}\ (for\ ideal\ engine)$$

$$\eta = 1 - \frac{373K}{1073K} = 0.652$$

$$W = \eta Q_h = 0.652 x 1 kilowatt - hr = 0.652 kilowatt - hr$$

b) For a perfect engine how much energy is discarded at the cold end for 1 MJ of energy extracted from the hot source. (4)

$$Given\ Q_h = 1MJ\ \ what\ is\ Q_c$$

$$Since\ 1 - \frac{Q_c}{Q_h} = \eta\ ;\ \frac{Q_c}{Q_h} = 1 - \eta\ ;\ Q_c = (1-\eta)Q_h$$

$$Q_c = (1 - 0.652)1MJ = 0.348MJ$$

c) Calculate the net change in entropy in (b).(2)

$$\Delta S = -\frac{Q_h}{T_h} + \frac{Q_c}{T_c} = 0$$

$$If\ \ I\ \ calculate\ \ ihe\ \ individual\ \ terms\ \ there\ \ are\ \ round - off\ \ errors$$

$$= -\frac{1MJ}{1073K} + \frac{0.348MJ}{373K}$$

$$= +1J/K \approx 0$$