Each problem is worth 25 pts each. <u>Show all work</u> (**Note:** Data page at back of exam)

1.) A 1.388 mol sample of ice at 273.15 K is added to 8.326 moles of water at 360 K at constant pressure (1 bar) in an adiabatic container. Calculate ΔS for this process. Is it spontaneous? (Base your answer on ΔS_{univ}) $\Delta \bar{H}^{\circ}_{fus}$ of water is 6.008 kJ mol^{-1}. Assume $\bar{C}_P$ is independent of temperature.

Find the final T : $q_{ice} + q_{water} = 0$ (adiabatic)

$$n_{ice}\Delta \bar{H}^{\circ}_{fus} + n_{ice}\bar{C}_{p(\ell)}(T_F - 273.15) + n_w \bar{C}_{p(\ell)}(T_F - 360) = 0$$

$$(1.388)(6.008 \times 10^3) + (1.388)(75.3)(T_F - 273.15) + (8.326)(75.3)(T_F - 360) = 0$$

$$T_F = 336.2 \ K$$

$$\Delta S_{sys} = \Delta S_{ice} + \Delta S_w = \frac{n_{ice}\Delta \bar{H}_{fus}}{T_{fus}} + n_{ice}\bar{C}_{p(\ell)}\ln\frac{T_F}{T_i} + n_w\bar{C}_{p(\ell)}\ln\frac{T_F}{T_i}$$

$$= \frac{(1.388)(6.008 \times 10^3)}{273.15} + (1.388)(75.3)\ln\frac{336.2}{273.15} + (8.326)(75.3)\ln\frac{336.2}{360}$$

$$= 9.35 \ J \ K^{-1}$$

$\Delta S_{surr} = 0$ (adiabatic)

$\Delta S_{univ} = \Delta S_{total} = +9.35 \ J \ K^{-1}$ > 0

$\Rightarrow$ spontaneous

2.) The standard enthalpy of dissociation for hypobromous acid, i.e., ΔH_r° for the reaction $HOBr(g) \rightarrow OH(g) + Br(g)$, has been measured to be 206.8 kJ mol^{-1} at 25°C.

(a) Determine the standard internal energy change ΔU_r° for this reaction.

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + RT\Delta n_{gas} \qquad \Delta n_{gas} = +1$$

$$\Delta U_r^\circ = \Delta H_r^\circ - RT$$

$$= 206.8 - (8.3145 \times 10^{-3})(298.15)$$

$$= 204.3 \ kJ/mol$$

(b) Calculate the standard Gibbs energy of dissociation, ΔG_r°, at 25°C.

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ$$

$$\Delta S_r^\circ = S^\circ(OH) + S^\circ(Br) - S^\circ(HOBr)$$

$$= (183.71) + (175.02) - (250) = 108.73 \ J \ K^{-1}$$

$$\Delta G_r^\circ = 206.8 - (298.15)(108.73 \times 10^{-3})$$

$$= 174.4 \ kJ/mol$$

(c) Determine the standard enthalpy of formation, ΔH_f°, for HOBr(g) at 25°C.

$$\Delta H_r^\circ = 206.8 = \Delta H_f^\circ(OH) + \Delta H_f^\circ(Br) - \Delta H_f^\circ(HOBr)$$

$$\Delta H_f^\circ(HOBr) = 38.99 + 111.86 - 206.8$$

$$= -55.95 \ kJ/mol$$

3.) The Haber synthesis for ammonia is $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. For an initial reactant mixture ratio of 2:1 (2 mol of N_2 : 1 mol H_2), it is found that 10% of the initial N_2 has reacted at equilibrium when the total pressure is 1.23 bar and T=500 K.

(a) Determine the value of the equilibrium constant K_P.

	N_2	H_2	NH_3
initial	2	1	0
equil	$2-X$	$1-3X$	$2X$
X_i	$\dfrac{2-X}{3-2X}$	$\dfrac{1-3X}{3-2X}$	$\dfrac{2X}{3-2X}$

total $= 3 - 2X$

$X = (0.1)2 = 0.2$ and $P = 1.23$ bar

$$K_P = \frac{\left(X_{NH_3}P\right)^2}{\left(X_{N_2}P\right)\left(X_{H_2}P\right)^3}$$

$$= \frac{\left(\frac{2X}{3-2X}\right)^2}{\left(\frac{2-X}{3-2X}\right)\left(\frac{1-3X}{3-2X}\right)^3}\cdot\frac{1}{P^2} = \frac{\left(\frac{0.4}{2.6}\right)^2}{\left(\frac{1.8}{2.6}\right)\left(\frac{0.4}{2.6}\right)^3(1.23)^2} = 6.21$$

(b) Determine ΔG_r^0 at 500 K.

$$\Delta G_r^0 = -RT\ln K_P = -(8.3145)(500)\ln 6.21 = -7591 \text{ J/mol}$$

(c) At 450 K, K_P increases to 87.5. Is this reaction exothermic or endothermic? Defend your answer.

easy way: Le Chatelier: decreasing T will shift equilibrium in the exothermic direction. Since K_P increases with decreasing T, rxn shifted towards products $\Rightarrow$ exothermic

long way:

$$\ln\frac{87.5}{6.21} = \frac{-\Delta H_r^0}{R}\left(\frac{1}{450}-\frac{1}{500}\right)$$

$$\Delta H_r^0 = -99.0 \text{ kJ/mol} \quad \therefore \text{ exothermic}$$

4.) (a) Show that $\left(\dfrac{\partial H}{\partial P}\right)_T = V(1-T\beta)$, where β is the coefficient of thermal expansion.

$$dH = TdS + VdP$$

divide by dP at const. T:

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T$$

$$= -\left(\frac{\partial V}{\partial T}\right)_P \quad \text{from Maxwell relation}$$

but $\beta = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P$

so $\left(\dfrac{\partial H}{\partial P}\right)_T = -TV\beta + V = V(1-T\beta)$

(b) Starting from the expression of part (a), calculate the change in molar enthalpy for liquid benzene at 25°C when the pressure is raised from 1 to 1000 bar (isothermally). The coefficient of thermal expansion for benzene is 1.237 x 10⁻³ K⁻¹, its density at this temperature is 0.879 g cm⁻³, and its molar mass is 78.11 g mol⁻¹. (You can safely assume that the density and β are independent of P.)

$$\overline{V} = \frac{1}{\rho} = \frac{1\,cm^3}{0.879\,g} \times \frac{78.11\,g}{mol} \times \left(\frac{1m}{100cm}\right)^3 = 8.8862 \times 10^{-5}\ m^3/mol$$

$$\Delta\overline{H} = \int_{P_1}^{P_2} \overline{V}(1-T\beta)\,dP = \overline{V}(1-T\beta)\Delta P \quad (\text{at const. } T)$$

$$= \left(8.8862 \times 10^{-5}\right)\left(1-(298.15)(1.237 \times 10^{-3})\right)\left(1000 \times 10^5 - 1 \times 10^5\right)$$

$$= 5.60 \times 10^3\ J/mol$$

(c) What is $\Delta\overline{G}$ for the process of part (b) ?

$$dG = -SdT + VdP \qquad \text{so} \qquad \left(\frac{\partial \overline{G}}{\partial P}\right)_T = \overline{V}$$

$$\Delta\overline{G} = \overline{V}\Delta P = \left(8.8862 \times 10^{-5}\right)\left(999 \times 10^5\right)$$

$$= 8.88 \times 10^3\ J/mol$$

DATA PAGE

$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1}$

$1 \text{ atm} = 101.325 \text{ kPa} = 760 \text{ Torr} = 1.01325 \text{ bar } (1 \text{ bar} = 10^5 \text{ Pa}); \quad 1 \text{ L} = 1 \text{ dm}^3$

$$\mu_{J-T} = \left(\frac{\partial T}{\partial P}\right)_H \quad , \quad \left(\frac{T_f}{T_i}\right) = \left(\frac{V_f}{V_i}\right)^{1-\frac{C_p}{C_v}} \quad , \quad w = -nRT \ln\frac{V_f}{V_i}$$

$$\frac{d\ln K_P}{dT} = \frac{\Delta H_r^o}{RT^2} \qquad\qquad \left(\frac{d(\Delta G/T)}{dT}\right)_P = -\frac{\Delta H}{T^2}$$

Maxwell relations:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Selected thermodynamic data at 298.15 K.

	$\Delta \bar{H}_f^o$ (kJ mol^{-1})	$\bar{S}^\circ$ (J K^{-1} mol^{-1})	$\bar{C}_P$ (J K^{-1} mol^{-1})
H$_2$O(l)	−285.8		75.3
OH(g)	38.99	183.71	
Br(g)	111.86	175.02	
HOBr(g)		250	