Physical Chemistry Cumulative Examination
11/03/11
R. P. Burns

1. [4] In an adiabatic system, if work is done by the system, how must the temperature change? Explain.

2. [4] One mole of an ideal gas expands irreversibly from a volume of 5.00 liters to a volume of 20.0 liters at a constant temperature of 3000 K. Calculate ΔS for this process.

3. [4] At 25 ºC the molar entropy of diamond is 2.38 J K^{-1} and the molar entropy of tin is 44.8 J K^{-1}. Calculate the difference in the entropies of these two substances as T → 0 K. Explain any assumptions involved in your calculation.

4. [4] A certain reaction has an equilibrium constant of 10 at 300 K and 100 at 400 K. Calculate the ratio of ΔGº at 300 K to ΔGº at 400 K

5. [4] A system exists under adiabatic conditions and at constant volume. What state function will be at a minimum when this system is at equilibrium? Explain your answer.

6. [4] A closed vessel contains $H_2O(\ell)$, $H_2O(g)$ and Ar(g). As the pressure of the Ar(g) in the vessel increases at constant temperature (298 K), what happens to the equilibrium vapor pressure of H_2O?

7. [4] If n_A moles of liquid A are mixed isothermally with n_B moles of liquid B to form an ideal solution, which of the following sets of quantities would we expect to have all zero values?
   a. ΔV, ΔH, q
   b. ΔS, ΔG, ΔV
   c. q, ΔH, ΔG
   d. ΔS, ΔH, ΔV
   e. q. ΔV. ΔG

8. [4] If ΔH^o for a reaction is independent of *T*, prove that ΔS^o for the reaction is independent of *T*.

9 . [25] Calculate ΔH^o, ΔS^o and ΔG^o for the conversion of 2 moles of liquid water at 110.0 ºC to gaseous water at 110.0 ºC at a constant pressure of 1 atm. Describe the reasoning behind your method. Data for H_2O at 1 atm are given below.

10. [25] 2.00 mol of an ideal gas undergoes each of the following processes:
   a. a reversible constant pressure expansion from (1.00 atm, 20.0 L) to (1.00 atm, 40.0 L);
   b. a reversible constant volume change in state from (1.00 atm, 40.0 L) to (0.500 atm, 40.0 L).
   c. a reversible isothermal compression (0.500 atm, 40.0 L) to (1.00 atm, 20.0 L).

   Calculate *q*, *w*, Δ*U*, Δ*H* and Δ*S* for process a, b and c.
   Sketch each process on one *P*-*V* diagram.
   Calculate *q*, *w*, Δ*U*, Δ*H* and Δ*S* for a cycle that consists of steps a. b. and c.

11. [18] Summarize the research topic, author and important conclusions presented in one physical chemistry seminar given in the Fall 2011 semester.

Information

$$dU \equiv \delta q + \delta w \qquad \delta w = -P_{ext}\, dV$$

$$dU = TdS - PdV + \sum_{i=1}^{K} \mu_i dn_i \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$H \equiv U + PV$$

$$dH = TdS + VdP + \sum_{i=1}^{K} \mu_i dn_i \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$A \equiv U - TS$$

$$dA = -SdT - PdV + \sum_{i=1}^{K} \mu_i dn_i \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \left(\frac{\partial (A/T)}{\partial T}\right)_V = -\frac{U}{T^2}$$

$$G \equiv H - TS$$

$$dG = -SdT + VdP + \sum_{i=1}^{K} \mu_i dn_i \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \left(\frac{\partial (G/T)}{\partial T}\right)_P = -\frac{H}{T^2}$$

$$dU = C_V dT - \left\{\left[\mu C_P + V\right]\left(\frac{\partial P}{\partial V}\right)_T + P\right\} dV$$

$$dH = C_P dT - \mu C_P dP \qquad \left(\frac{\partial H}{\partial T}\right)_P = C_P$$

$$C_P - C_V = -\left\{\left(\frac{\partial H}{\partial P}\right)_{T,n} - V\right\}\left(\frac{\partial P}{\partial T}\right)_V \qquad C_P - C_V = -\left\{\left(\frac{\partial U}{\partial V}\right)_{T,n} + P\right\}\left(\frac{\partial V}{\partial T}\right)_P$$

$$dS = \frac{dq_{rev}}{T} \qquad dS = \left[\frac{nC_v^m}{T}\right] dT + \left\{\left(\frac{1}{T}\right)\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\right\} dV$$

$$\ln f = \ln P + \frac{1}{RT}\int_0^P \left[V_m - \frac{RT}{P}\right] dP \qquad G = \mu^o + RT \ln f$$

R	=	8.3145 J mol^{-1} K^{-1}	1 newton (N) = 1 kg m s^{-2}
	=	0.083145 L bar mol^{-1} K^{-1}	1 N m^{-2} = 1 Pa
	=	83.145 cm^3 bar mol^{-1} K^{-1}	1 N m = 1 joule (J)
	=	82.058 cm^3 atm mol^{-1} K^{-1}	1 atm = 101325 Pa
	=	0.082058 L atm mol^{-1} K^{-1}	1 torr = 1/760 atm = 133.322 Pa
	=	1.9872 cal mol^{-1} K^{-1}	1 bar = 10^5 Pa = 0.986923 atm = 750.062 torr
N_A	=	6.02214 x 10^{23} mol^{-1}	1 cal = 4.184 J
k	=	1.38066 x 10^{-23} J K^{-1}	
h	=	6.62608 x 10^{-34} J s	Zero of the Celcius scale = 273.15 K

C_V (ideal monatomic gas) = 3/2 R

f = c – p + 2 (no reactions)

Data for H_2O at 1 atm:

ΔH^o_{fusion} (0 °C) = 6.010 kJ mol^{-1} $\quad$ $\Delta H^o_{vaporization}$ (100 °C) = 41.0 kJ mol^{-1}

C_P(s) = 38.0 J mol^{-1} K^{-1} $\quad$ $C_P(\ell)$ = 75.0 J mol^{-1} K^{-1} $\quad$ C_P(g) = 34.0 J mol^{-1} K^{-1}

ρ(H_2O(*s*) = 0.9168 g cm^{-3} $\quad$ ρ(H_2O(*l*) = 0.9998 g cm^{-3}

Molecular mass of H_2O = 18.015 amu