

CY 102: Physical Chemistry
End Semester
May 3, 2004

Answer All Questions

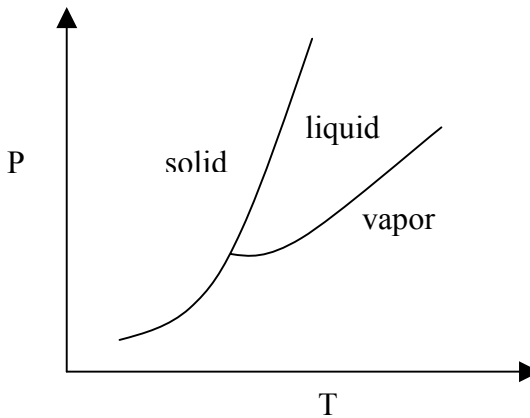
$$R = (8.314 \text{ J} = 0.0821 \text{ atm dm}^3) \text{ K}^{-1} \text{ mol}^{-1}$$

$$\text{Trouton's constant} = 88 \text{ J K}^{-1} \text{ mol}^{-1}$$

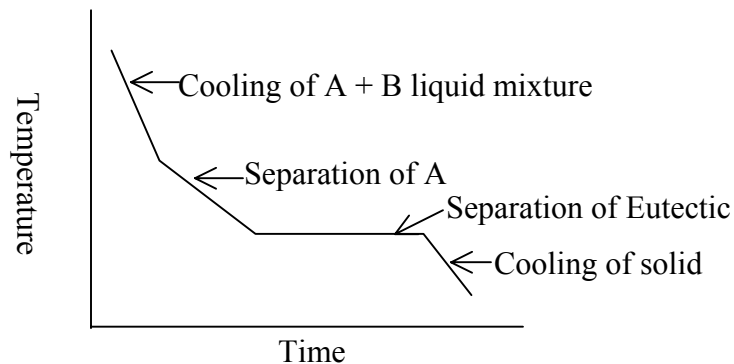
$$F = 96,500 \text{ C mol}^{-1}$$

Question 1: Fill in the blanks

- (a) For free expansion of a gas, $\Delta S_{\text{surr}} = \underline{\text{Zero}}$ and $\Delta S_{\text{system}} = \underline{\text{Positive}}$ (Choose from: positive, negative, zero)
- (b) The enthalpy of vaporization of water is $186.5 \text{ kJ mol}^{-1}$. Its entropy of vaporization is $\underline{500 \text{ J mol}^{-1} \text{ K}^{-1}}$.
- (c) For a one-component system the molar volume of the liquid phase is larger than the molar volume of the solid phase. Its pressure versus Temperature phase diagram is



- (d) For the reversible compression of an isolated ideal gas at 298K to a volume half of its initial volume, the change in molar entropy (in joule units) is Zero.
- (e) Substance A and B form an eutectic mixture at 100°C with a molar composition A:B = 3:2. The schematic cooling curve of an intimate mixture of 5 moles of A and 2 moles of B is



- (f) For a third order reaction $3A \rightarrow \text{products}$, the time taken for 75% change in the concentration of A is 5 times that for 50% change.
- (g) The rate law, $d[D]/dt$ for the mechanism $A \rightleftharpoons B$; $B + C \rightarrow D$, using SSA to the intermediate, is $d[D]/dt = k_1 k_2 [A][C] / k_{-1} + k_2 [C]$.
- (h) The emf of the cell $\text{SCE} // \text{H}^+(\text{aq})/\text{Q}, \text{H}_2\text{Q} / \text{Pt}$ is 0.16V at 298K. Given $E_{\text{SCE}} = 0.242\text{V}$ and $E^0(\text{H}_2\text{Q}/\text{Q}) = 0.699\text{V}$, the pH of the aqueous solution is 5.
- (i) Consider the cell reaction $\text{Cu}(\text{s}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$ at 298K. If the concentration for Cu^{2+} is 1.0M and the emf of the cell is zero, the concentration of Ag^+ is $1.65 \times 10^{-8} \text{M}$. (Given $E^0(\text{Cu}^{2+}/\text{Cu}) = 0.34\text{V}$ and $E^0(\text{Ag}^+/\text{Ag}) = 0.80\text{V}$)
- (j) Reaction $A + B \rightarrow P$ is first order with respect to each reactant. Given $[A]_0 = 0.10\text{M}$, $[B]_0 = 6.0\text{M}$ and $k = 5.0 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$, the concentration of a remaining at $t = 100\text{s}$ is $4.98 \times 10^{-3} \text{M}$.

Question 2:

- (a) Ammonium hydrosulphide decomposes according to the reaction,



ΔG^0 for this reaction at 300K is 6198J mol^{-1} . Some solid NH_4HS is placed in an evacuated vessel at 300K. What is the pressure of $\text{NH}_3(\text{g})$ at equilibrium?

$$\text{Ans: } \Delta G^0 = -RT \ln K_p; \quad K_p = e^{-\Delta G^0/RT} = e^{-(6198/(8.314 \times 300))} = 0.0833$$

$$K_p = P_{\text{NH}_3} \cdot P_{\text{H}_2\text{S}} = p^2 = 0.0833$$

$$P_{\text{NH}_3} = \sqrt{0.0833} = 0.289 \text{ atm.}$$

- (b) The boiling point of a normal liquid is 127°C at 1 atm. Estimate the vapour pressure of the liquid (in atm unit) at 27°C and 1 atm total pressure.

$$\text{Ans: } \Delta H_v^0 = \text{Troutons constant} \times \text{Boiling temperature} = 88 (273+127) = 35200 \text{Jmol}^{-1}$$

$$\ln P_2/P_1 = -\Delta H_v^0/R (1/T_2 - 1/T_1) \text{ (Clausius Clayperon)}$$

$$\ln P_2 = -35200/8.314 (1/300 - 1/400) = -3.528$$

$$P_2 = 0.0294 \text{ atm.}$$

- (c) A reversible heat engine absorbs 40 kJ of heat at 500K, performs 10 kJ of work and rejects the remaining heat to the sink at 300 K. Calculate the entropy change of the universe.

$$\text{Ans: } \Delta S (\text{source}) = -40000/500 = -80 \text{ JK}^{-1}$$

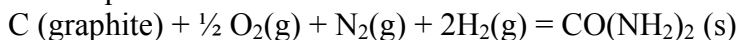
$$\Delta S (\text{sink}) = 30000/300 = 100 \text{ JK}^{-1}$$

$$\Delta S(\text{univ}) = (-80+100) \text{ JK}^{-1} = 20 \text{ JK}^{-1}.$$

(d) Using the data given, calculate the standard Gibbs free energy of formation of urea, $\text{CO}(\text{NH}_2)_2$.



Ans: Equation for formation of urea:



Accordingly from the above equations:

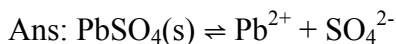
$$\Delta G^0(\text{formation}) = \Delta G_1^0 + \Delta G_2^0/2 + \Delta G_3^0 + \Delta G_4^0 = 2562.15 \text{ Jmol}^{-1}$$

(e) State True (T) or False (F) in the space provided:

- (i) The efficiency of Carnot heat engine depends on the heat capacity of the working substance. [F]
- (ii) For an ideal gas at constant pressure, the graph of H versus T and G versus T will always have opposite slopes [T]
- (iii) For a substance with different allotropic forms at constant pressure, an increase in temperature favours the stability of the allotrope with higher entropy [T].
- (iv) $(\partial U/\partial V)_s = P$ – [F]

Question 3:

(a) Estimate the solubility product of PbSO_4 at 298 K. Given $E^0(\text{Pb}^{2+}/\text{Pb}) = -0.125\text{V}$ and E^0 of the half-cell $\text{SO}_4^{2-}(\text{aq}) / \text{PbSO}_4(\text{s}) / \text{Pb}(\text{s})$ is -0.356V .



$$E_{\text{cell}}^0 = -0.356 - (-0.125) = -0.231 \text{ V}$$

$$n = 2$$

$$\log_{10} K_{\text{sp}} = nE_{\text{cell}}^0/0.0591$$

$$= 2(-0.231)/0.0591 = -7.8173$$

$$K_{\text{sp}} = 1.52 \times 10^{-8}$$

(b) For the cell reaction $\text{Zn} + \text{Cu}^{2+}(1\text{M}) \rightarrow \text{Zn}^{2+}(1\text{M}) + \text{Cu}$, $\Delta H^0 = -218.5 \text{ kJ mol}^{-1}$ at 298K. Given $E^0(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$ and $E^0(\text{Cu}^{2+}/\text{Cu}) = 0.34\text{V}$, calculate the temperature coefficient, $(\partial E^0/\partial T)_p$ of the cell.

$$\text{Ans: } \Delta G^0 = -nFE^0 = -2 \times 96500 \times 1.10 = -212.3 \text{ KJ mol}^{-1}$$

$$\Delta H^0 = -218.5 \text{ kJ mol}^{-1} \text{ (Given)}$$

$$\Delta S^0 = \Delta H^0 - \Delta G^0/T = -20.80 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta S^0 = nF (\partial E^0/\partial T)_p$$

$$(\partial E^0/\partial T)_p = -1.08 \times 10^{-4} \text{ VK}^{-1}$$

(c) The activation energy for the decomposition of HL is 184 kJ mol^{-1} . By what factor the number of effective collisions increases if the temperature is increased from 500K to 700K?

$$\begin{aligned} \text{Ans: } \log_e k_2/k_1 &= E_a/R [T_2 - T_1/T_1T_2] \\ &= 184 \times 10^3/8.314 (200 / 500 \times 700) = 12.6 \\ k_2/k_1 &= 3.1 \times 10^5. \end{aligned}$$

(d) An enzyme has a turnover number of $1 \times 10^4 \text{ min}^{-1}$. If 6.67 (or 20/3) moles of substrate is turned-over per hour per gram of the enzyme when the substrate concentration is twice the Michaelis constant, calculate the molar mass of the enzyme.

$$\begin{aligned} \text{Ans: } \# &= k_2[E]_0 [S]_0/k_m + [S]_0 = 2/3 k_2[E]_0 \quad \because k_m = 1/2 [S]_0 \\ 20/3 \times 1/60 &= 2/3 \times 1 \times 10^4 \times 1/M \\ M &= 6 \times 10^4 \text{ g mol}^{-1}. \end{aligned}$$

(e) For a parallel first order reaction $B \leftarrow A \rightarrow C$, derive the expression for the concentration of B at any time t.

$$\begin{aligned} \text{Ans: } d[B]/dt &= k_1[A] = k_1[A]_0 e^{-k't} \\ \int d[B] &= \int k_1[A]_0 e^{-k't} \\ [B] &= -k_1[A]_0/k' e^{-k't} + \text{constant} \\ \text{At } t = 0, [B] &= 0; \\ \text{Constant} &= +k_1[A]_0/k_1 [1 - e^{-k't}] \\ (\text{where } k' &= k_1 + k_2) \end{aligned}$$

Question 4:

Calculate the entropy change of the universe when an aluminum block of 500 gm mass and total heat capacity at constant pressure of 496.2 J K^{-1} at 100°C , is placed in a lake of water temperature 10°C .

$$\begin{aligned} \text{Ans: Heat rejected to lake} &= 496.2 (100 - 10) \text{ J} \\ \Delta S_{\text{lake}} &= 496.2 \times 90 / 283.15 = 157.72 \text{ JK}^{-1} \\ \Delta S_{\text{block}} &= nC_p \ln T_2/T_1 = -496.2 \ln 373.15 / 283.15 = -136.95 \text{ JK}^{-1} \\ \Delta S_{\text{univ}} &= (157.72 - 136.95) \text{ JK}^{-1} = 20.77 \text{ JK}^{-1}. \end{aligned}$$

(Note: The mass of block is not used in calculation. It is simply to imply that the lake is too large and its temperature will not rise because of the block).

Question 5:

The equilibrium constant for the reaction $2\text{HL} \rightleftharpoons \text{H}_2 + \text{L}_2$ is 1.7×10^{-2} at 400°C and 2.2×10^{-2} at 500°C . If ΔH^0 remains constant during this temperature interval, calculate ΔS^0 at 400°C .

Ans: $\ln K_2/K_1 = -\Delta H^0/R (1/T_1 - 1/T_2)$ (Van't Hoff's eqn.)

$$\ln (2.2 \times 10^{-2} / 1.7 \times 10^{-2}) = -\Delta H^0 / 8.314 (1/773 - 1/673)$$

$$\Delta H^0 = 11151 \text{ J mol}^{-1}$$

$$\Delta G^0 (400^\circ\text{C}) = -RT \ln (1.7 \times 10^{-2}) = 35682 \text{ J mol}^{-1}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\text{so, } \Delta S^0 (400^\circ\text{C}) = \Delta H^0 - \Delta G^0 / T$$

$$= 11151 - 35682 / 673 = -36.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

Question 6:

The melting point of bismuth (Atomic mass 209) is 271°C . At this temperature, the density of solid bismuth is 9.673 kg dm^{-3} and liquid bismuth is 10.0 kg dm^{-3} respectively. The melting point falls by 0.00354 degree when the pressure is increased by 1 atm. calculate the latent heat of fusion of bismuth.

Ans: $dP/dT = \Delta S/\Delta V = \Delta H/T\Delta V$

$$\Delta V = V_l - V_s = (1/10 - 1/9.673) \text{ dm}^3 \text{ kg}^{-1} = -3.3805 \times 10^{-3} \text{ dm}^3 \text{ kg}^{-1}$$

$$= \{-3.3805 \times 10^{-3}\} \times 209 \text{ dm}^3 \text{ mol}^{-1} = -0.7065 \text{ dm}^3 \text{ mol}^{-1}$$

$$\Delta H = dP/dT \cdot T\Delta V = 1/(-0.00354) \times .554 \times (-0.7065)$$

$$= 108.57 \text{ kJ mol}^{-1}$$

Question 7:

The solubility of methyl amine at 298K in water is 8.5 times higher than in chloroform. Calculate the percentage of the base that remains in 1000 ml of chloroform if it is extracted (i) four times, always with 200 ml of water and (ii) twice with 400 ml of water.

Ans:

$$(i) \quad x_4 = 100 (K_D V_0 / V_1 + K_D V_0)^4 \%$$

$$K_D = 1/8.5, V_0 = 1000 \text{ ml}, V_1 = 200 \text{ ml}, x_4 = 1.9\%$$

$$(ii) \quad V_1 = 400 \text{ ml}$$

$$x_2 = 100 ((1/8.5)(1000) / 400 + (1/8.5)(1000)) = 5.2\%$$

Question 8:

A mole of helium initially at 300K & 10 atm was heated to 600K and the final pressure of the gas was adjusted to 100 atm. Calculate ΔG for the process assuming ideal behaviour of He. Given $S_{298K}^0 = 126 \text{ JK}^{-1} \text{ mol}^{-1}$.

Ans: $C_p (\text{He}) = 5/2 R, \quad n = 1$

$$\Delta G = \Delta G_1 (300\text{K}, 10\text{atm} \rightarrow 300\text{K}, 1\text{atm})$$

$$+ \Delta G_2 (300\text{K}, 1\text{atm} \rightarrow 600\text{K}, 1\text{atm})$$

$$+ \Delta G_3 (600\text{K}, 1\text{atm} \rightarrow 600\text{K}, 100\text{atm})$$

$$\Delta G_1 = nRT \ln 1/10 = -5742.83 \text{ J}$$

$$\begin{aligned}
\Delta G_2 &= \Delta H - (T_2 S_2 - T_1 S_1) \\
&= C_p \Delta T - 600 (S^0 + C_p \ln 600/298) + 300 (S^0 + C_p \ln 300/298) \\
&= 6235 - 84921.4 + 37838.57 = -40247.33 \text{ J} \\
\Delta G_3 &= RT \ln 100/1 = 22971.33 \text{ J} \\
\Delta G_{\text{total}} &= -5742.83 - 40247.33 + 22971.33 \\
&= -23018.83 \text{ J.}
\end{aligned}$$

Question 9:

A solution of A is mixed with an equal volume of a solution of B containing the same number of moles and the reaction $A + B \rightarrow C$ occurs. At the end of 1 h, A is 75% reacted. How much of A will be left unreacted at the end of 2 h, if the reaction is (a) first order in A and zero order in B (b) first order in both A and B and (c) zero order in both A and B?

Ans: (a) 1st order in A zero order in B: 100 75%/1h 25 75%/1h 6.25
(or) $t_{3/4} = 2 t_{1/2} = 1\text{h} \quad \therefore t_{1/2} = 30 \text{ min}$
In 2h, 4 $t_{1/2}$, amt. remaining = $(1/2)^4 = 1/16$ i.e., 6.25%.

(b) $R = K[A]^1 [B]^0 / K = 1/t \cdot x/a(a-x) = 75 / 100 \times 25 = 3/100 \text{ M}^{-1}\text{h}^{-1}$.
 $x / a - x = K \text{ at } = 3/100 \times 100 \times 2 = 6$
 $\therefore (a - x) = 14.29\%$

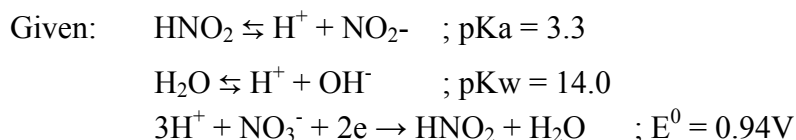
(c) $R = K$ 0% remaining.

Question 10:

A certain unimolecular reaction proceeds by a direct path (i) as well as by a catalysed path (ii) E_a for path (i) exceeds that of path (ii) by 20 KJ mol⁻¹. The rate of path (ii) is 36 times more than that of path (i) at 300 K. How the entropy of activation is modified in the presence of the catalyst?

$$\begin{aligned}
\text{Ans: } k_{\text{cat}} / k_{\text{uncat}} &= e^{(\Delta S_c^\ddagger - \Delta S_{\text{uc}}^\ddagger)/R} \cdot e^{(E_{\text{uc}} - E_c)/RT} \\
36 &= e^x \cdot e^{20 \times 10^3 / 8.314 \times 300} \\
&= e^{(x + 8.0186)} \\
x + 8.0186 &= 3.5835 \\
x &= -4.4351 \\
\Delta S_c^\ddagger - \Delta S_{\text{uc}}^\ddagger / R &= -4.4351 \\
\Delta S_c^\ddagger - \Delta S_{\text{uc}}^\ddagger &= -36.87 \text{ JK}^{-1} \text{ mol}^{-1}. \\
\Delta S^\ddagger &\text{ decreases by } 36.87 \text{ JK}^{-1} \text{ mol}^{-1}.
\end{aligned}$$

Question 11:



Compute the half-cell potential for the reaction $\text{NO}_3^- + \text{H}_2\text{O} + 2e \rightarrow \text{NO}_2^- + 2\text{OH}^-$ at 298K.

$$\begin{aligned} \text{Ans: } \Delta G^\ominus &= \Delta G^\ominus_{\text{①}} + 2\Delta G^\ominus_{\text{②}} + \Delta G^\ominus_{\text{③}} \\ &= 2.303 RT \text{pK}_a + 2(2.303 RT \text{pK}_w) - 2F(0.94) \\ &= 2.303 RT (\text{pK}_a + 2\text{pK}_w) - 181420 \\ &= 2.303 \times 8.314 \times 298 \times 31.3 - 181420 \\ &= 178593 - 181420 \\ &= -2826.95 \text{ J mol}^{-1} \\ E^0 &= -\Delta G^0/nF = 2826.95 / 2 \times 96500 = 0.015 \end{aligned}$$

Question 12:

25.0ml of 0.24 M Cu^+ is titrated with 0.05M $\text{Cr}_2\text{O}_7^{2-}$ solution in a cell SCE// redox mixture / Pt. Calculate the emf of the cell, when (i) 10.0 ml of $\text{Cr}_2\text{O}_7^{2-}$ solution is added and (ii) 20.0 ml of $\text{Cr}_2\text{O}_7^{2-}$ is added. Assume $[\text{H}^+] = 1.0\text{M}$. Given $E^0 (\text{Cu}^{2+}/\text{Cu}^+) = 0.153\text{V}$; $E^0 (\text{Cr}_2\text{O}_7^{2-} / \text{Cr}^{3+}) = 1.33\text{V}$; $E_{\text{SCE}} = 0.242 \text{ V}$.

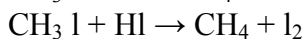
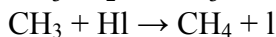
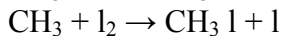
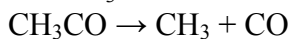
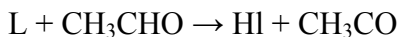
Ans: (i) Normality of $\text{Cu}^+ = 0.24$; $\text{Cr}_2\text{O}_7^{2-} = 0.30 \text{ N}$
M equivalents of $\text{Cu}^+ = 6$; milliequivalents of $\text{Cr}_2\text{O}_7^{2-} = 3$
This corresponds to 50% of equivalence point

$$\begin{aligned} \therefore E^0 \text{ Cu}^{2+} / \text{Cu}^+ &= 0.153 \text{ V} \\ \therefore E_{\text{cell}} &= 0.153 - 0.242 = -0.089 \text{ V}. \end{aligned}$$

(iii) milliequivalents of $\text{Cr}_2\text{O}_7^{2-} = 6$
This corresponds to equivalence point
 $\therefore E_{\text{eq}} = n_1 E^0_1 + n_2 E^0_2 / n_1 + n_2$
 $= 1(0.153) + 6(1.33) = 1.162 \text{ V}$
 $\therefore E_{\text{cell}} = 1.162 - 0.242 = 0.92 \text{ V}$.

Question 13:

The proposed mechanism for the decomposition of ethanal catalysed by iodine is given by $\text{I}_2 \rightleftharpoons 2\text{I}$



Derive an expression for the rate of formation of CO.

$$\text{Ans: (i) } d[\text{CO}]/dt = k_3[\text{CH}_3\text{CO}]$$

$$\text{(ii) } d[\text{CH}_3\text{CO}]/dt = k_2[\text{I}][\text{CH}_3\text{CHO}] - k_3[\text{CH}_3\text{CO}] = 0$$

$$[\text{CH}_3\text{CO}] = k_2[\text{I}][\text{CH}_3\text{CHO}] / k_3$$

$$\text{(iii) } d[\text{I}]/dt = 2k_1[\text{I}_2] - 2k_{-1}[\text{I}]^2 - k_2[\text{I}][\text{CH}_3\text{CHO}] + k_4[\text{CH}_3][\text{I}_2] + k_5[\text{CH}_3][\text{HI}] = 0$$

$$(iv) \frac{d[CH_3]}{dt} = k_3[CH_3CO] - k_4[CH_3][I_2] - k_5[CH_3][HI] = 0$$

Adding (ii) + (iii) + (iv)

$$2k_1[I_2] = 2k_{-1}[I]^2$$

$$(v) [I] = (k_1[I_2]/k_{-1})^{1/2}$$

$$(vi) \text{ From (ii) } k_3[CH_3CO] = k_2[I][CH_3CHO]$$

$$\begin{aligned} \therefore \frac{d[CO]}{dt} &= k_2[CH_3CHO][I] \\ &= k_2[CH_3CHO](k_1[I_2]/k_{-1})^{1/2} \\ &= k_2(k_1/k_{-1})^{1/2}[CH_3CHO][I_2]^{1/2} \end{aligned}$$