PHYSICAL CHEMISTRY

EXAM Ⅲ (6/12/2014) Dept. Chem. & Biol. Eng., Korea Univ. Prof. D. J. Ahn

1.[40]두 휘발성 액체 A, B의 평형 혼합물에 대해 다음을 계산하시오.

(a:5) 혼합물이 Ideal solution과 같이 행동할 때 $\triangle_{mix}G$, $\triangle_{mix}S$, $\triangle_{mix}H$ 를 구하시오.

(b:5) 혼합물이 Regular solution ($H^E \neq 0, S^E = 0$)과 같이 행동할 때, $\triangle_{mix}G$, $\triangle_{mix}S$, $\triangle_{mix}H$ 를 구하시오. (Suppose that the excess enthalpy depends on composition as $H^E = n\beta RTx_Ax_B$).

(c:10) 그림 1과 그림 2를 보고 β의 값에 따른 A, B의 mixing 거동에 대해 설명하고, 각 phase들의 조성을 예측하시오. (혼합에 관한 임계값이 $\beta = 2$ 임을 수학적으로 증명하면 추가점수 부여.)

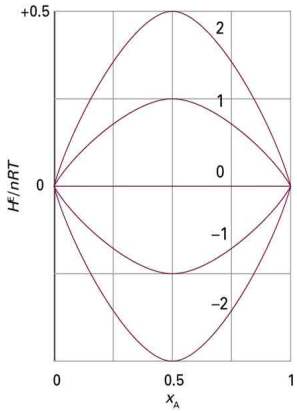


그림 1

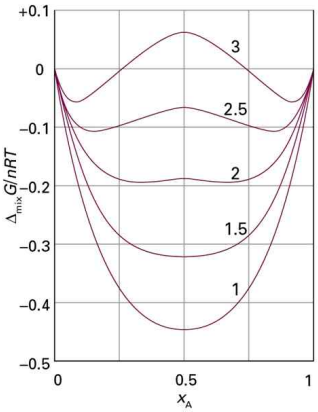


그림 2

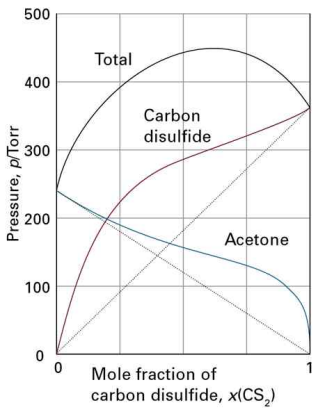


그림 3

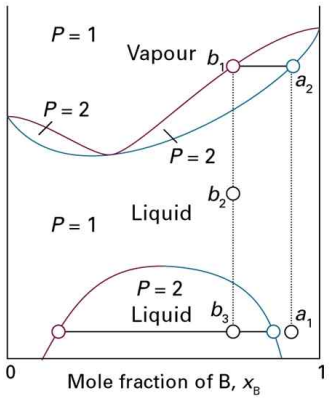


그림 4

(d:10) Acetone−Carbon disulfide 혼합물에서 β 값의 변화에 따라 partial pressure curve들에 미치는 영향을 설명하시오.

(e:10) 두 액체 A, B의 상평형 그림이 일정한 압력에서 그림 3과 같을 때 어떤 성분이 더 휘발성인지 말하고, 각 영역에서의 DOF를 구하시오. 액체 혼합물 a_1의 온도를 $T_1 \rightarrow T_2 \rightarrow T_3 \rightarrow T_1$의 순서로 변화시킨다. 첫 단계에서 마지막 단계(총 4단계)까지 존재하는 모든 상들의 조성을 구하시오. [※점 a_1에서 x_B = 0.90, 점 b_1에서 x_B = 0.70] 액체혼합물 a_1에서 A의 조성이 높은 액체를 추출하기 위한 방법을 제안하시오.

2[10]. An et al. investigated the liquid-liquid coexistence curve of N,Ndimethylacetamide and heptane. Mole fractions of N,Ndimethylacetamide in the upper (X_1) and lower (X_2) phases of a two region are given below as a function of temperature:

T/K	309.820	309.422	309.031	308.006	306.686	304.553	301.803	299.097	296.00	294.534
X_1	0.473	0.400	0.371	0.326	0.293	0.255	0.218	0.193	0.168	0.157
X_2	0.529	0.601	0.625	0.657	0.690	0.724	0.758	0.783	0.804	0.814

(a) Plot the phase diagram. (b) State the proportions and compositions of the two phases that form from mixing 0.750 mol of N,Ndimethylacetamide with 0.250 mol of heptane at 296.0 K. To what temperature must the mixture be heated to form a single mixture?

3[10]. Starting from the equilibrium between a solvent (A) and a solution (A+B) separated by a semipermeable membrane, derive the van't Hoff equation Π = [B]RT, where Π is the osmotic pressure and [B] is the molar concentration of the solute B.

4[10]. The degree of dissociation, α, of CO_2(g) into CO(g) and O_2(g) at high temperatures was found to vary with temperature as follows:

T/K	1395	1443	1498
$\alpha/10^{-4}$	1.44	2.50	4.71

Assuming $\triangle_r H^{\ominus}$ to be constant over this temperature range, calculate K, $\triangle_r G^{\ominus}$, $\triangle_r H^{\ominus}$ and $\triangle_r S^{\ominus}$. Make any justifiable approximations.

5[30]. Given the cell, $Zn(s)|ZnCl_2(aq)\|CuCl_2(aq)|Cu(s)$ at 25℃, of which electrolyte concentrations are $m(CuCl_2)=1.0\times10^{-3}$ mol/kg and $m(ZnCl_2)=5.0\times10^{-3}$ mol/kg (m is the molality), answer the followings:

(a) the half-cell reactions at cathode and anode, and the overall cell reaction.

(b) the standard cell potential (E^{θ}) and the equilibrium constant K.

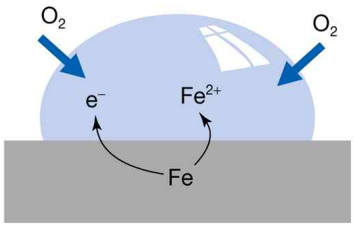
(c) the ionic strengths (I) of the two electrolyte solutions.

(d) the mean ionic activity coefficients ($\gamma_{\pm}$), using the Debye-Hückel limiting law.

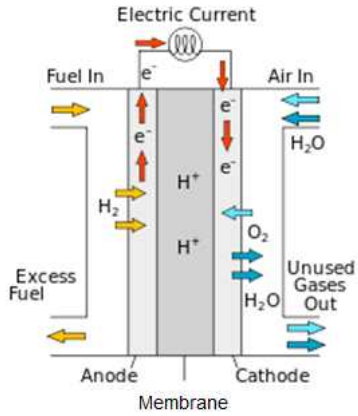
$$\log\gamma_{\pm} = -0.509|z_- z_+|I^{1/2},\quad I=\frac{1}{2}\sum z_i^2(b_i/b^{\ominus}).$$

(e) the reaction quotient (Q) and the cell potential (E).

6[15]. (a) 철의 부식과정은 아래의 그림과 같다. 이 때 부식을 방지하는 방법을 복수로 제안하시오.
(b) 연료전지(fuel cell)의 연료로 수소기체를 사용할 경우, 각 전극에서의 반쪽 반응식과 전체 전지 반응식을 쓰고 표준 전위를 구하시오. 현재, 연료전지의 성능개선에 관한 이슈를 설명하시오.

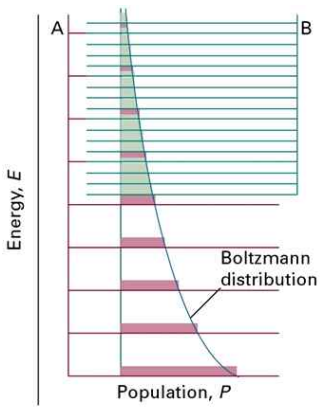


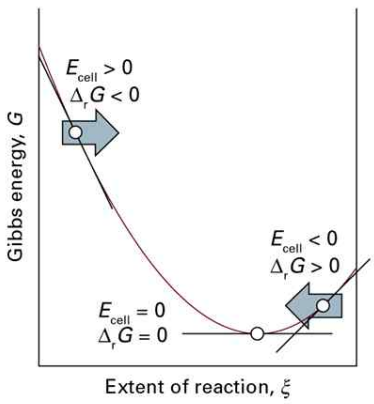
(a)



(b)

7[15]. $A\leftrightarrow 2B$ 반응에 대한 Boltzmann distribution을 왼쪽 그림에 나타내었다. 오른쪽 그림은 $\triangle_r G$ 에 따라 반응 진행 방향을 설명하고 있다. 이 두 그림과 Le Chatelier principle을 고려하여 온도 및 압력의 증감이 반응에 미치는 영향을 설명하시오.





8[20]. 다음을 설명하시오. (3~5줄)

(a) chemical potential (b) entropy (c) reversible process (d) $G=f(T,P,...)$일 때 dG의 표현식과 그 활용

(총 150점) 한 학기동안 수고 많았습니다.

Table 10.7 Standard potentials at 298 K. (a) In electrochemical order

Reduction half-reaction	$E^\ominus$/V
Strongly oxidizing	
$H_4XeO_6 + 2H^+ + 2e^- \longrightarrow XeO_3 + 3H_2O$	+3.0
$F_2 + 2e^- \longrightarrow 2F^-$	+2.87
$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O$	+2.07
$S_2O_8^{2-} + 2e^- \longrightarrow 2SO_4^{2-}$	+2.05
$Ag^{2+} + e^- \longrightarrow Ag^+$	+1.98
$Co^{3+} + e^- \longrightarrow Co^{2+}$	+1.81
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	+1.78
$Au^+ + e^- \longrightarrow Au$	+1.69
$Pb^{4+} + 2e^- \longrightarrow Pb^{2+}$	+1.67
$2HClO + 2H^+ + 2e^- \longrightarrow Cl_2 + 2H_2O$	+1.63
$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	+1.61
$2HBrO + 2H^+ + 2e^- \longrightarrow Br_2 + 2H_2O$	+1.60
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.51
$Mn^{3+} + e^- \longrightarrow Mn^{2+}$	+1.51
$Au^{3+} + 3e^- \longrightarrow Au$	+1.40
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+1.33
$O_3 + H_2O + 2e^- \longrightarrow O_2 + 2OH^-$	+1.24
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.23
$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + H_2O$	+1.23
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	+1.23
$Br_2 + 2e^- \longrightarrow 2Br^-$	+1.09
$Pu^{4+} + e^- \longrightarrow Pu^{3+}$	+0.97
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+0.96
$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$	+0.92
$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$	+0.89
$Hg^{2+} + 2e^- \longrightarrow Hg$	+0.86
$NO_3^- + 2H^+ + e^- \longrightarrow NO_2 + H_2O$	+0.80
$Ag^+ + e^- \longrightarrow Ag$	+0.80
$Hg_2^{2+} + 2e^- \longrightarrow 2Hg$	+0.79
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77
$BrO^- + H_2O + 2e^- \longrightarrow Br^- + 2OH^-$	+0.76
$Hg_2SO_4 + 2e^- \longrightarrow 2Hg + SO_4^{2-}$	+0.62
$MnO_4^{2-} + 2H_2O + 2e^- \longrightarrow MnO_2 + 4OH^-$	+0.60
$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	+0.56
$I_2 + 2e^- \longrightarrow 2I^-$	+0.54
$Cu^+ + e^- \longrightarrow Cu$	+0.52
$I_3^- + 2e^- \longrightarrow 3I^-$	+0.53
$NiOOH + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-$	+0.49
$Ag_2CrO_4 + 2e^- \longrightarrow 2Ag + CrO_4^{2-}$	+0.45
$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$	+0.40
$ClO_4^- + H_2O + 2e^- \longrightarrow ClO_3^- + 2OH^-$	+0.36
$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$	+0.36
$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	+0.27
$AgCl + e^- \longrightarrow Ag + Cl^-$	+0.22
$Bi^{3+} + 3e^- \longrightarrow Bi$	+0.20
$Cu^{2+} + e^- \longrightarrow Cu^+$	+0.16
$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+0.15
$AgBr + e^- \longrightarrow Ag + Br^-$	+0.07
$Ti^{4+} + e^- \longrightarrow Ti^{3+}$	0.00
$2H^+ + 2e^- \longrightarrow H_2$	0, by definition
$Fe^{3+} + 3e^- \longrightarrow Fe$	−0.04
$O_2 + H_2O + 2e^- \longrightarrow HO_2^- + OH^-$	−0.08
$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.13
$In^+ + e^- \longrightarrow In$	−0.14
$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.14
$AgI + e^- \longrightarrow Ag + I^-$	−0.15
$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.23
$Co^{2+} + 2e^- \longrightarrow Co$	−0.28
$In^{3+} + 3e^- \longrightarrow In$	−0.34
$Tl^+ + e^- \longrightarrow Tl$	−0.34
$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$	−0.36
$Ti^{3+} + e^- \longrightarrow Ti^{2+}$	−0.37
$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.40
$In^{2+} + e^- \longrightarrow In^+$	−0.40
$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	−0.41
$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.44
$In^{3+} + 2e^- \longrightarrow In^+$	−0.44
$S + 2e^- \longrightarrow S^{2-}$	−0.48
$In^{3+} + e^- \longrightarrow In^{2+}$	−0.49
$U^{4+} + e^- \longrightarrow U^{3+}$	−0.61
$Cr^{3+} + 3e^- \longrightarrow Cr$	−0.74
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.76
$Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^-$	−0.81
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	−0.83
$Cr^{2+} + 2e^- \longrightarrow Cr$	−0.91
$Mn^{2+} + 2e^- \longrightarrow Mn$	−1.18
$V^{2+} + 2e^- \longrightarrow V$	−1.19
$Ti^{2+} + 2e^- \longrightarrow Ti$	−1.63
$Al^{3+} + 3e^- \longrightarrow Al$	−1.66
$U^{3+} + 3e^- \longrightarrow U$	−1.79
$Sc^{3+} + 3e^- \longrightarrow Sc$	−2.09
$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.36
$Ce^{3+} + 3e^- \longrightarrow Ce$	−2.48
$La^{3+} + 3e^- \longrightarrow La$	−2.52
$Na^+ + e^- \longrightarrow Na$	−2.71
$Ca^{2+} + 2e^- \longrightarrow Ca$	−2.87
$Sr^{2+} + 2e^- \longrightarrow Sr$	−2.89
$Ba^{2+} + 2e^- \longrightarrow Ba$	−2.91
$Ra^{2+} + 2e^- \longrightarrow Ra$	−2.92
$Cs^+ + e^- \longrightarrow Cs$	−2.92
$Rb^+ + e^- \longrightarrow Rb$	−2.93
$K^+ + e^- \longrightarrow K$	−2.93
$Li^+ + e^- \longrightarrow Li$	−3.05