

## 익힘문제 해답

### 1장\_열역학 제1법칙

**1.2** (a) 불완전  $\because \frac{\partial M}{\partial y} = e^y \neq \frac{\partial N}{\partial x} = e^y + 1$

(b) 완전  $\because \frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} = 1$

모함수  $f(x,y)$ :  $f = \int M dx + g(y) = x^2 + xy + g(y);$

$$\frac{\partial f}{\partial y} = x + 2y = x + \frac{dg}{dy}, \quad \therefore g(y) = \int 2y dy = y^2 + C$$

따라서  $f = x^2 + xy + y^2 + C$ . 여기서  $C$ 는 적분상수.

(c) 완전  $\because \frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} = e^x$ ;

모함수  $f(x,y)$ :  $f = \int N dy = (1 + e^x)y + g(x);$

$$\frac{\partial f}{\partial x} = e^x y + \frac{dg}{dx} = e^x(y - x), \quad \therefore g = -\int xe^x dx + C = e^x(1 - x) + C$$

(d) 완전  $\because \frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} = 6xy^2$

모함수  $f(x,y)$ :  $f = \int M dx + g(y) = \frac{2}{5}x^5 + x^2y^3 + g(y)$

$$\frac{\partial f}{\partial y} = 3x^2y^2 + \frac{dg}{dy} = 3y^2(x^2 + y^2), \quad \therefore g = \int 3y^4 dy = \frac{3}{5}y^5 + C$$

**1.3**  $dV = \left(\frac{\partial V}{\partial r}\right)_h dr + \left(\frac{\partial V}{\partial h}\right)_r dh = 2\pi rh dr + nr^2 dh; \frac{\partial^2 V}{\partial h \partial r} = \frac{\partial^2 V}{\partial r \partial h} = 2\pi r$

**1.4** (a)  $dV = \left(\frac{db}{dT} + \frac{R}{P}\right)dT - \frac{RT}{P^2}dP$  (b)  $\frac{\partial^2 V}{\partial P \partial T} = \frac{\partial^2 V}{\partial T \partial P} = -\frac{R}{P^2}$

### 2장\_열역학 제1법칙

**2.4** (b) (아래 계산 값에서  $R = 0.08205 \text{ L} \cdot \text{atm/mol}$ )

경로 (i):  $w = 75.0 R; \Delta U = 112.5 R; q = 187.5 R; \Delta H = 187.5 R$

경로 (ii):  $\Delta U = 0; q = w = RT_2 \ln(V_3/V_2) = (373 \ln 2)R; \Delta H = 0$

경로 (iii):  $q = 0; w = -\Delta U = 112.5 R; \Delta H = C_p \Delta T = -187.5 R$

**2.5**  $P\Delta V = (1 \text{ atm})(1674 - 1 \text{ cm}^3) = 40.51 \text{ cal}$  (물 1g의 부피를 1 cm<sup>3</sup>로 가정)

**2.6** (a)  $w = P\Delta V = 731 \text{ cal}; \Delta U = q - w = 9730 - 731 = 8999 \text{ cal}; \Delta H = q = 9730 \text{ cal}$

(b)  $\Delta U = q = 8999 \text{ cal}; \Delta H = q = 9730 \text{ cal}$

(c)  $w = P\Delta V = -0.0395 \text{ cal}; \Delta H = q = 1436 \text{ cal}; \Delta U = q - w = 1436 \text{ cal}$

**2.7**  $T_f = 235.6 \text{ K}; q = 0; -\Delta U = w = 144.0 R = 1.20 \text{ kJ/mol}; \Delta H = \Delta U + \Delta(PV) = -201.6 R = -1.68 \text{ kJ/mol}$

**2.8** (a)  $T_f = 271.4 \text{ K}, P = 110.5 \text{ kPa}$  (b)  $T_f = 277.9 \text{ K}, P = 107.9 \text{ kPa}$

**2.9** (a)  $w = RT(1 - P'/R) + RT(1 - P_2/P')$  (b)  $dw/dP' = 0, \therefore P' = \sqrt{P_1 P_2}$

(c)  $w_{\max} = 2RT(1 - \sqrt{P_2/P_1})$

**2.10** (a)  $P-V$  면에서  $V = 10 \text{ L}$ ,  $P = 10 \text{ atm}$ 을 중심으로 하는 반경이 5인 원

(b)  $w = 25\pi \text{ L} \cdot \text{atm} = 7958 \text{ J} = q \because \Delta U = 0$

(c)  $T_{\max} = (10 + 5/\sqrt{2})^2/R = 2233 \text{ K}; T_{\min} = (10 - 5/\sqrt{2})^2/R = 509 \text{ K}$

### 3장\_열역학 제2법칙

**3.3** (a)  $\int_{V_1}^{V_2} \delta q_{irr}/T = 0 \because \delta q_{irr} = 0$ ; (b)  $\int_{V_1}^{V_2} \delta q_{rev}/T = \int_{V_1}^{V_2} (P/T)dV/T = R \ln(V_2/V_1)$

**3.4** (b)  $w = C(\sqrt{T_2} - \sqrt{T_1})^2$

**3.5** (a) 냉장고:  $\eta_R = |q_c| / |w| = T_c / (T_h - T_c)$ ; 열펌프:  $\eta_P = |q_h| / |w| = T_h / (T_h - T_c)$

(b)  $w = q_c / \eta_R = 79.71 \text{ kcal} / (273 \text{ K} / 30 \text{ K}) = 8.76 \text{ kcal}$

**3.6** (b) 678.6 K

**3.7** (a)  $w = w_{ab} + w_{cd} = (P_{ab} - P_{cd})(V_b - V_a)$ ; (b)  $T_{cd} > T_{ab}$

(c)  $w = q_{cd}(T_{cd} - T_{ab})/T_{cd}$ ; (d)  $\Delta T/T_{cd}\Delta P = -0.0906 \text{ cm}^3/79.8 \text{ cal} = -2.75 \times 10^{-5}/\text{atm}$

**3.8** (a)  $\oint \frac{\delta q}{T} = \int_{\text{1단계}} \frac{\delta q}{T} + \int_{\text{2단계}} \frac{\delta q}{T} = 0 - R \ln 2 < 0$ ; (b)  $\Delta S = -R \ln 2$ ; (c)  $\Delta S = R \ln 2$ ; (d)  $\Delta S = R \ln 2 q/T = 0$

**3.9**  $\Delta S = mgh/T = (1 \text{ kg})(9.80 \text{ m/s}^2)(1 \text{ m})/(273.15 \text{ K}) = 0.0359 \text{ J/K}$

**3.10** (a)  $\Delta H_{Hg} = -2099.4 \text{ J}; \Delta S_{Hg} = -6.29 \text{ J/K}$  (b)  $\Delta H_w = 2099.4 \text{ J}; \Delta S_w = 7.08 \text{ J/K}$

(c)  $\Delta H = \Delta H_{Hg} + \Delta H_w = 0; \Delta S = \Delta S_{Hg} + \Delta S_w = 0.79 \text{ J/K} > 0$

### 4장\_엔트로피의 물리적 의미

**4.1** 정압조건일 때  $\delta q_{rev} = dH$

**4.2** (a) 1몰이라고 하면,  $\Delta S/R = \ln(V_2/V_1) = \Delta \ln \Omega_{\text{conf}} < 0$

(b)  $\Delta S/R = \Delta \ln \Omega_{\text{th}} + \Delta \ln \Omega_{\text{conf}} = C_v \ln(T_2/T_1) + R \ln(V_2/V_1) = 0$

**4.3** (a)  $\Omega_{200}(100) = \frac{200!}{100! \times 100!}$

**4.4** (a)  $q = 1 + e^{-\varepsilon/kT}; \lim_{T \rightarrow 0} q = 1, \lim_{T \rightarrow \infty} q = 2$  ( $q$ 는 주어진 온도에서 한 개의 입자가 있을 수 있는 미시상태의 수에 해당).

(b)  $P(0) = \frac{1}{q}; P(\varepsilon) = \frac{e^{-\varepsilon/kT}}{q}$

(c)  $U = 0 \cdot P(0) + \varepsilon \cdot P(\varepsilon) = \frac{\varepsilon}{(1 + e^{\varepsilon/kT})}; \lim_{T \rightarrow 0} U = 0, \lim_{T \rightarrow \infty} U = \frac{\varepsilon}{2}$

(d)  $\frac{S}{k} = -[P(0) \ln P(0) + P(\varepsilon) \ln P(\varepsilon)]$

**4.5** (a)  $\Delta S = R \ln 4$  (b)  $\Delta S = R \ln 8$  (c)  $\Delta S = R \ln(32/27)$

**4.6**  $\Delta S/R = 0.186$

### 5장\_보조함수

**5.3** (a)  $\Delta U = 0; \Delta H = 0; \Delta S = R \ln 2; \Delta F = \Delta U - T\Delta S = -RT \ln 2; \Delta G = \Delta H - T\Delta S = -RT \ln 2$

(b)  $\Delta U = C_V(T_2 - T_1); \Delta H = C_p(T_2 - T_1); \Delta S = S_2 - S_1 = C_p \ln(T_2/T_1) - R \ln(P_2/P_1);$

$\Delta F = \Delta U - T_2 \Delta S - (T_2 - T_1)S_1; \Delta G = \Delta H - T_2 \Delta S - (T_2 - T_1)S_1$

- (c)  $\Delta U = C_V(T_2 - T_1)$ ;  $\Delta H = C_p(T_2 - T_1)$ ;  $\Delta S = S_2 - S_1 = C_p \ln(T_2/T_1)$ ;  
 $\Delta F = \Delta U - T_2 \Delta S - (T_2 - T_1)S_1$ ;  $\Delta G = \Delta H - T_2 \Delta S - (T_2 - T_1)S_1$
- (d)  $\Delta U = C_V(T_2 - T_1)$ ;  $\Delta H = C_p(T_2 - T_1)$ ;  $\Delta S = S_2 - S_1 = C_V \ln(T_2/T_1)$ ;  
 $\Delta F = \Delta U - T_2 \Delta S - (T_2 - T_1)S_1$ ;  $\Delta G = \Delta H - T_2 \Delta S - (T_2 - T_1)S_1$
- 5.4** (a)  $\Delta H = 10.21 \text{ L} \cdot \text{atm/mol}$  (b)  $\Delta U = 0.0523 \text{ L} \cdot \text{atm/mol}$  (c)  $\Delta G = 10.27 \text{ L} \cdot \text{atm/mol}$   
(d)  $\Delta F = 0.0052 \text{ L} \cdot \text{atm/mol}$  (e)  $\Delta S = -1.962 \times 10^{-4} \text{ L} \cdot \text{atm/mol} \cdot \text{K}$
- 5.5**  $q = \Delta H = 296 \text{ cal/g}$ ;  $\Delta U = \Delta H - P\Delta V = 266 \text{ cal/g}$ ;  $\Delta S = \Delta H/T = 1.02 \text{ cal/gK}$ ;  $\Delta F = \Delta U - T\Delta S = -30 \text{ cal/g}$ ;  $\Delta G = 0$
- 5.6** (a)  $G_B - G_A = \int_A^B \left( \frac{\partial G}{\partial P} \right)_T dP = \int_A^B V dP$ ;  $F_B - F_A = \int_A^B \left( \frac{\partial F}{\partial V} \right)_T dV = - \int_A^B P dV$   
(b)  $(G_B - G_A) - (F_B - F_A) = \int_A^B V dP + \int_A^B P dV = \int_A^B d(PV) = P_B V_B - P_A V_A$   
(c)  $\Delta G = \Delta F + \Delta(PV)$

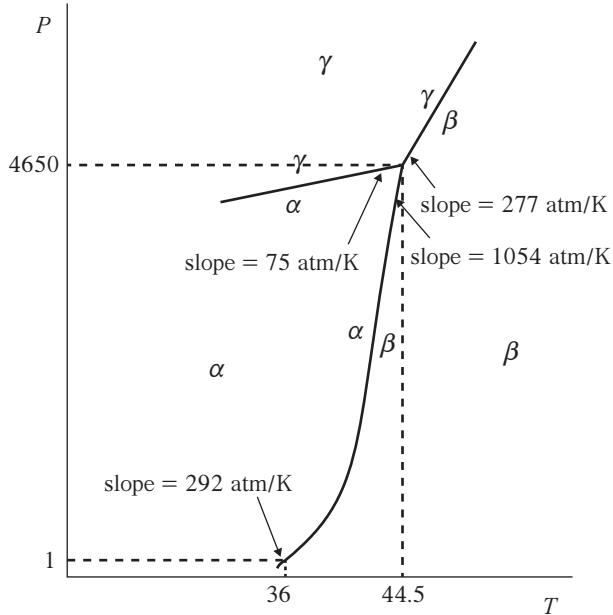
## 6장\_열용량

- 6.1** (a)  $q = 1 + e^{-\beta\varepsilon}$  (b)  $U = \langle \varepsilon \rangle = \frac{\varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}}$  (c)  $C_V = -\frac{1}{kT^2} \frac{\partial U}{\partial \beta} = k \left( \frac{\varepsilon}{kT} \right)^2 \frac{e^{-\varepsilon/kT}}{(1 + e^{-\varepsilon/kT})^2}$   
(d)  $\lim_{T \rightarrow \infty} C_V = k$ ;  $\lim_{T \rightarrow 0} C_V = 0$
- 6.2**  $S_{368.5}(\text{monoclinic}) - S_0(\text{rhombic}) = (8.810 \pm 0.05) + (0.261 \pm 0.002) = 9.07 \pm 0.05 \text{ cal/mol} \cdot \text{K}$ ;  
 $S_{368.5}(\text{monoclinic}) - S_0(\text{monoclinic}) = 9.04 \pm 0.10 \text{ cal/mol} \cdot \text{K}$ . 이들이 실험오차 범위에서 서로 같으므로,  
 $S_0(\text{monoclinic}) = S_0(\text{rhombic})$ .  $S_0(\text{rhombic}) = 0^\circ$ 면,  $S_0(\text{monoclinic}) = 0$ .
- 6.3**  $\lim_{T \rightarrow 0} \left( \frac{\partial V}{\partial T} \right)_P = \lim_{T \rightarrow 0} \left( -\frac{\partial S}{\partial P} \right)_T = 0$  (i.e.,  $\alpha \rightarrow 0$ );  $\lim_{T \rightarrow 0} \left( \frac{\partial P}{\partial T} \right)_V = \lim_{T \rightarrow 0} \left( \frac{\partial S}{\partial V} \right)_T = 0$  (i.e.,  $\alpha \rightarrow 0$ )
- 6.4** (a)  $\Delta S_{\text{sys+surr}} = 22 \text{ cal/K}$  (b)  $w_{\text{ex}} \leq -\Delta G_{T,P} = -(\Delta H - T\Delta S) = 5485 \text{ cal}$
- 6.5** (a)  $\Delta H^0 = 66,752 \text{ J/mol}$  (b)  $\Delta S^0 = 157 \text{ J/mol} \cdot \text{K}$
- 6.6**  $\Delta H_{rxn}^o = -402.7 \text{ kcal/mol}$ ;  $\Delta S_{rxn}^o = -77.9 \text{ kcal/mol} \cdot \text{K}$ ;  $\Delta G_{rxn}^o = -270.3 \text{ kcal/mol}$
- 6.7** (a)  $x = 0.0426$  (b)  $\Delta S = 0.0056 \text{ J/K}$
- 6.8**  $T_f = 297.6 \text{ K}$
- 6.9** (a)  $T_f = 1597 \text{ K}$  (b)  $T_f = 1922 \text{ K}$

## 7장\_1성분계의 상평형

- 7.1** (b)  $\left( \frac{\partial \mu_c}{\partial P} \right)_T = v_c > 0$
- 7.2** 3169.5 Pa (0.071% 증가)
- 7.3** 언 물(얼음)로부터 승화 건조
- 7.4** (a)  $\Delta G(298 \text{ K}) = \Delta H - T\Delta S = 2.898 \text{ kJ/mol}$   
(b)  $\Delta G > 0$ 이므로 흡연  
(c)  $\Delta G_{\text{dia}} = V_{\text{dia}} \Delta P = 346.4 \text{ J/mol}$   
(d) 14,928 atm ( $\approx 15,000$  atm)  
(e)  $\Delta G(900\text{K}) = 4.921 \text{ kJ/mol}$
- 7.5** 1202 K (실제는 1180 K)
- 7.6** 온도를 올리기 전 0.0406, 올린 후 0.0532

- 7.7** (a) 194.6 K (b)  $p = 73.2 \text{ atm}$   
(c) 1 atm 하에서는 ice가 녹을 때 액체가  
생기지 않으므로  
(d) 73.2 atm (25°C에서 CO<sub>2</sub> 액체와 기체가  
공존할 때 평형 압력은 실제 67 기압)

**7.8****7.9** 909.2°C

## 8장\_혼합기체

**8.3**  $(\mu - \mu^o)/RT = \ln P$

**8.4**  $\Delta S = \int_{1L}^{2L} \left( \frac{\partial S}{\partial V} \right)_T dV = \int_{1L}^{2L} \left( \frac{\partial P}{\partial T} \right)_V dV = 0.71R;$

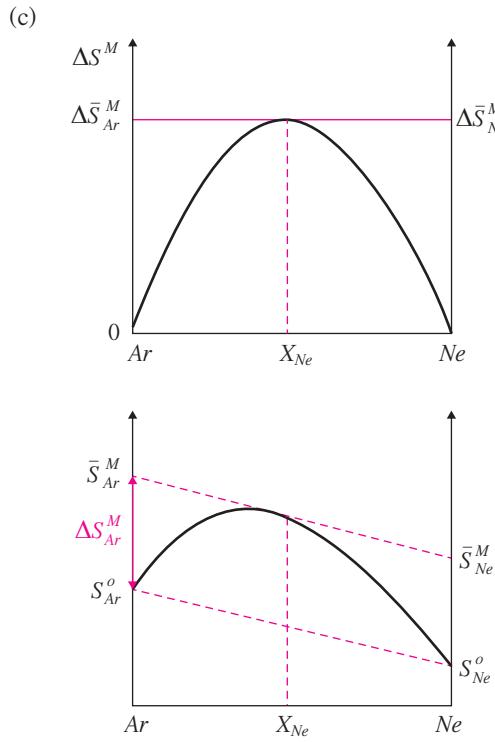
$$\Delta G = \int_{1L}^{2L} \left( \frac{\partial G}{\partial V} \right)_T dV = \int_{1L}^{2L} V \left( \frac{\partial P}{\partial V} \right)_T dV = -22.73 \text{ L} \cdot \text{atm/mol}$$

**8.5** (a)  $x = 1/2$  (b)  $\Delta \bar{G}_A^M = -RT \ln 2 = \Delta \bar{G}_B^M$  (c)  $P = 2 \text{ atm}$  (d)  $\Delta \bar{G}_A^M = 0 = \Delta \bar{G}_B^M$

**8.6** (a)  $\Delta G^M = RT \left( \frac{4}{12} \ln \frac{4}{12} + \frac{n}{12} \ln \frac{n}{12} + \frac{8-n}{12} \ln \frac{8-n}{12} \right)$  (b)  $n = 4$  (c)  $\Delta G^M = -(300 \ln 3)R$

**8.7** (a)  $\Delta \bar{S}_{Ar}^M = -R \ln 0.5 = 5.76 \text{ J/mol} \cdot \text{K}$

(b)  $\bar{S}_{Ar}^M = S_{298}^o(Ar) + \Delta \bar{S}_{Ar}^M = 154.72 + 5.76 = 160.48 \text{ J/mol} \cdot \text{K}$



## 9장\_용액열역학

**9.1** 0.467 atm

**9.2**  $RT \ln \gamma_{Cu} = -38.300x_{Zn}^2$

**9.3**  $a_{Bi} = 0.444$

**9.4** (a)  $\bar{V}_A^M = V_m - x_B \frac{dV_m}{dx_B} = 100 + 2.5x_B^2$ ,  $\bar{V}_B^M = V_m - x_A \frac{dV_m}{dx_A} = 80 + 2.5x_A^2$

(b)  $\Delta V^M = 2.5x_A x_B$

**9.5**  $x_B = 0.507$ .

**9.6** (a)  $\Delta T = 121$  K (b)  $\Delta S = 3.50$  cal/K

**9.7**  $\Delta T = 2.37$  K

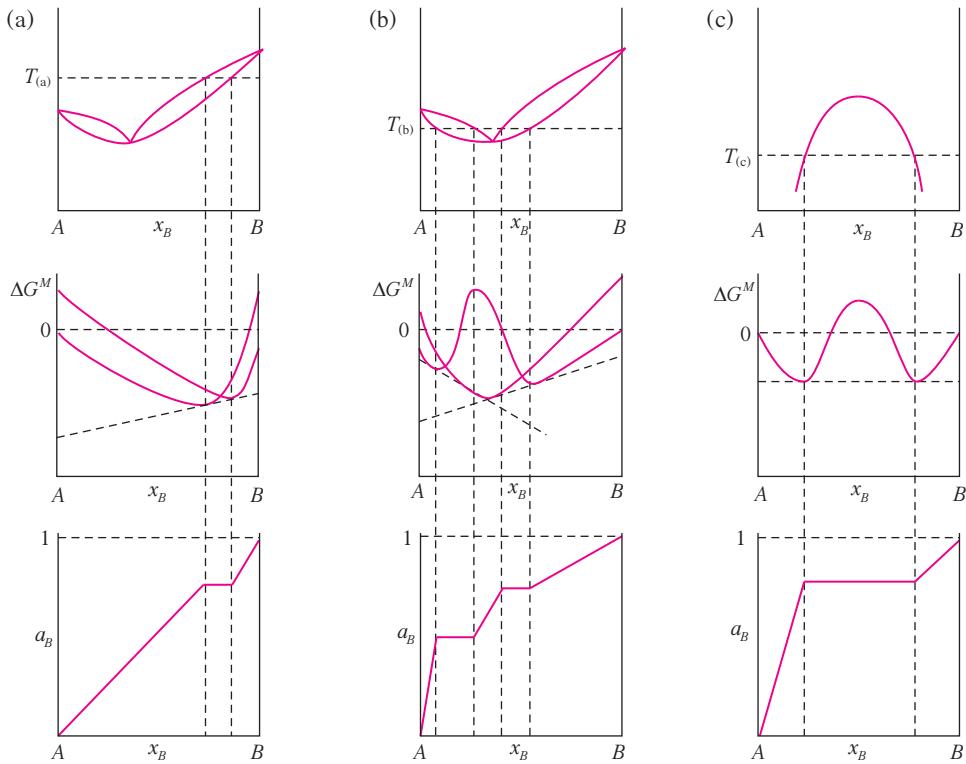
**9.8**  $\bar{G}_{Fe}^{M,xs} = \alpha x_{Ni}^2 = -870$  J/mol

**9.9** (a)  $\Delta H^M = 1606$  J (b)  $\Delta S_{sur} = -1.07$  J/K;  $\Delta S_{sys} = 11.94$  J/K

**9.10** (a)  $T_{cr} = \frac{\alpha_o + \beta P}{2R}$  (b)  $\partial T_{cr} / \partial P = \beta / 2R$

## 10\_2성분계의 섞임 자유에너지 대 조성 그림

10.1



10.2 (a)  $a_{B,l} = x_B e^{1.684x_A^2}$  (b,c)  $a_{B,s} = a_{B,l} \exp\left(\frac{G_{m,B}^o}{RT}\right) = 0.786 \cdot a_{B,l}$

10.4 (b)  $T_{m,A} = 1443$  K;  $T_{m,B} = 722$  K (c)  $T_E = 577$  K (d)  $x_B = 0.778$  (e) 9%으로.

10.5 (a)  $\Delta G^M = -11,140$  J/mol (b)  $\Delta G^M = 0$

10.6 MgO에서 CaO의 포화용해도  $x_{\text{CaO}} = 0.066$ ; CaO에서 MgO의 포화용해도  $x_{\text{MgO}} = 0.15$

10.7 (a) 2418 K (b)  $x_A = 0.62$  (c) 2444 K (d)  $x_A = 0.38$

10.8 (a)  $a_{\text{Fe},l} = 0.919$  (b)  $a_{\text{Fe},s} = 0.95$

## 11장\_기체끼리의 화학반응

11.1  $\Delta H^\circ = 888$  KJ  $R = 7.38$  kJ

11.2 (a) 1428 K (b) 164 atm.

11.3 (a)  $P_{\text{N}_2} = 0.2488$  atm;  $P_{\text{H}_2} = 0.7465$  atm;  $P_{\text{NH}_3} = 0.0047$  atm

(b)  $P_{\text{N}_2} = 0.4909$  atm;  $P_{\text{H}_2} = 1.4727$  atm;  $P_{\text{NH}_3} = 0.0182$  atm

11.4  $x_{\text{H}_2} = 0.198, x_{\text{CO}_2} = 0.198, x_{\text{CO}} = 0.552, x_{\text{H}_2\text{O}} = 0.052$

11.5  $\text{CO}_2/\text{H}_2 = 1.276$

11.6 (a)  $P_{\text{H}_2} = 1.05 \times 10^{-8}$  atm,  $P_{\text{O}_2} = 0.0756$  atm (b)  $P_{\text{H}_2} = 3.31 \times 10^{-8}$  atm,  $P_{\text{O}_2} = 0.756$  atm

## 12장\_응집상과 기상 간의 화학반응

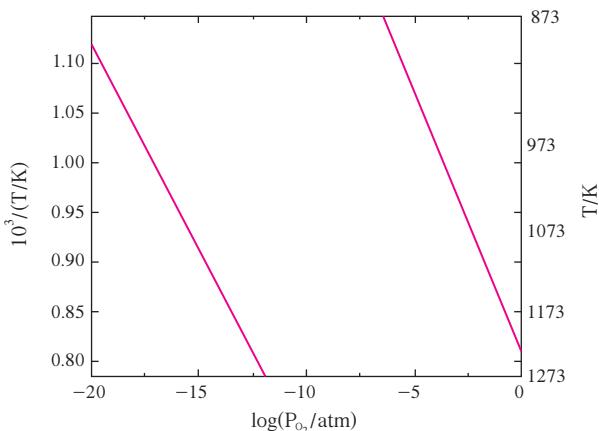
**12.1** (a)  $P_{O_2} = 1.12 \times 10^{-16}$  atm

**12.2** (a)  $K_{eq} = 3026$ ;  $\Delta H^\circ = -49.91$  kJ;  $\Delta G^\circ = -66.64$  kJ (b) NiO가 환원.

**12.3** (a)  $P_{SiO} = 8.14 \times 10^{-8}$  atm (b)  $\Delta H^\circ = 6.395 \times 10^5$  J;  $\Delta S^\circ = 309.9$  J/K (c)  $P_{O_2} = 10^{-32}$  atm

**12.4** (a)  $2H_2O_{(g)} + Si_{(s)} = SiO_{2(s)} + 2H_{2(g)}$  (b)  $K_{eq} = 2.88 \times 10^{13}$  (c) < 0.19 ppm

**12.5**



**12.6** CoO가 Co로 환원됨

**12.7**  $\Delta H_f^\circ = -37.215$  kJ/mol

**12.8**  $\Delta G^\circ$ 식을 위에서부터 차례대로 (i), (ii), (iii)으로 하면, (i)  $Mg_{(s)}$ , (ii)  $Mg_{(v)}$ , (iii)  $Mg_{(l)}$ ;  $T_m = 928$  K,  $\Delta H_m = 8.67$  kJ/mol,  $\Delta S_m = 9.34$  J/mol • K;  $T_b = 1372$  K,  $\Delta H_b = 133.92$  kJ/mol,  $\Delta S_b = 97.62$  J/mol • K.

**12.9** (a)  $\Delta H^\circ = 1.666 \times 10^5$  (b)  $T = 1168$  K (c)  $T = 1165$  K

(d) 이상기체 법칙에 의하여,  $P = 1.23$  atm

## 13장\_열역학의 응용: 몇 가지 예

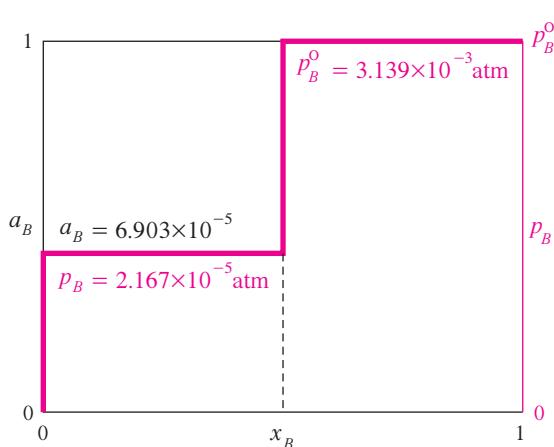
**13.2** 고상합금의 조성을  $A_xB_{1-x}$ , 산화물고용체의 조성을  $(AO)_y(BO)_{1-y}$ 라 하면,  $x = 0.294$ ,  $y = 0.929$

**13.3**  $a_{PbO} = 0.500$

**13.4** (a)  $\Delta G_{f,AB}^\circ = -31,978$  J/mol

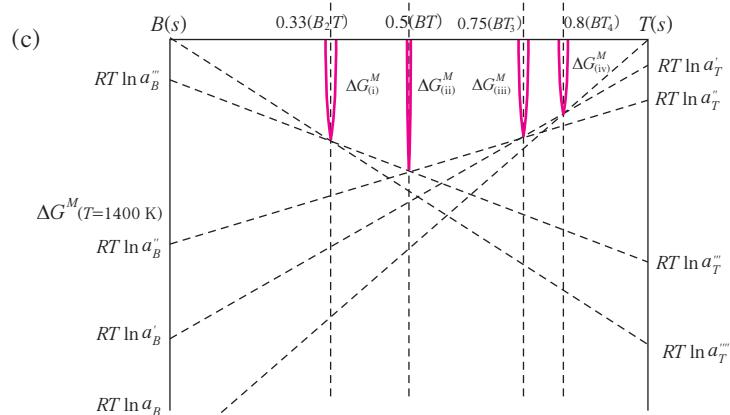
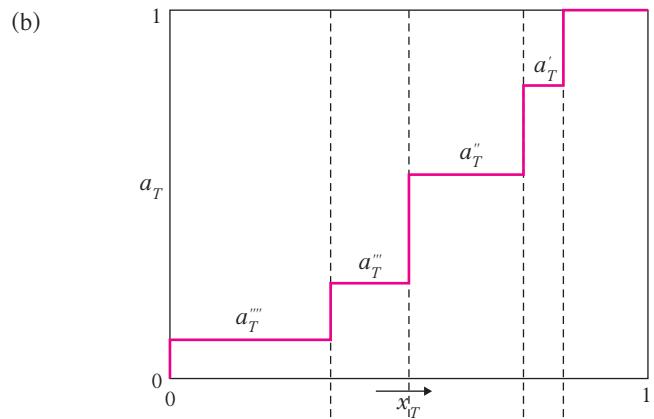
(b)  $a_A = a_B = a_{AB} = 1$

(c)



$$(d) a_A a_B = e^{\Delta G_{f,AB}^o / RT} = 0.0069$$

**13.5** (a) 압력이 일정한 계이므로, (i)  $F = 2$  (단일상영역); (ii)  $F = 1$  (두 상 영역); (iii)  $F = 0$  (삼 상 영역)



$$(d) a_B = 5.869 \times 10^{-3}; a_T = 5.557 \times 10^{-4}$$

**13.6**  $X_O = 8.19 \times 10^{-8}$  ( $= 0.0819$  ppm)

**13.7** (a)  $a_{\text{Fe}} = 0.0671$  (b)  $a_{\text{FeO}} = 0.791$