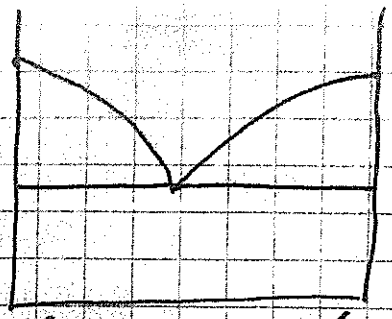
Question 1

Met 6208
Examen final
le 17 déc., 2003

Solutionnaire



$$\begin{cases} RT\ln a_{LaCl_3} = 3RT\ln X_{LaCl_3} + \omega X_{LaF_3}^2 = -(54392 - 48.092T) \\ RT\ln a_{LaF_3} = 3RT\ln X_{LaF_3} + \omega X_{LaCl_3}^2 = -(50208 - 28.430T) \end{cases}$$

$T = 654^\circ C = 927\,K$

$$\begin{cases} \ln(1-X_{LaF_3}) + \frac{\omega}{3(7706.7)} X_{LaF_3}^2 = (-1.273)/3 \\ \ln X_{LaF_3} + \frac{\omega}{3(7706.7)}(1-X_{LaF_3})^2 = (-3.095)/3 \end{cases}$$

$$f(X) = \frac{0.424}{X^2}\ln(1-X) - \frac{1.032}{(1-X)^2}\ln X = 0$$

X	f(X)
0.1	33.4
0.2	5.9
0.3	1.09
0.4	-0.86
0.32	0.61
0.38	-0.54
0.35	-0.01

$X_{LaF_3} = 0.35$

$\omega = (+994 \quad +1217)$ ave $= 1100$ J/mol

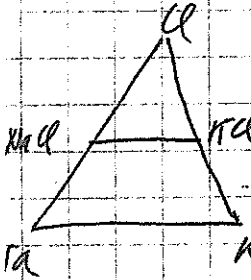
2005 (II) - Question 4

(i) $G = (n_{NaCl} g^\circ_{NaCl} + n_{KCl} g^\circ_{KCl}) + RT(n_{NaCl} \ln x_{NaCl} + n_{KCl} \ln x_{KCl}$

(ii) $G = (n_{Na} g^\circ_{Na} + n_K g^\circ_K + n_{Cl} g^\circ_{Cl})$

$$+ \left(\frac{\Delta g_{NaCl}}{2}\right) n_{Na-Cl} + \left(\frac{\Delta g_{KCl}}{2}\right)(n_{K-Cl}) + \left(\frac{\Delta g_{Na-K}}{2}\right)(n_{Na-K})$$

(n_{Na-Cl} = number of pairs)



$$+ RT(n_{Na} \ln x_{Na} + n_K \ln x_K + n_{Cl} \ln x_{Cl})$$

$$+ \frac{RT}{2}\left(n_{Na-Na} \ln \frac{x_{Na-Na}}{x_{Na}^2} + n_{K-K} \ln \frac{x_{K-K}}{x_K^2} + n_{Cl-Cl} \ln \frac{x_{Cl-Cl}}{x_{Cl}^2}\right.$$

$$\left. + n_{Na-Cl} \ln \frac{x_{Na-Cl}}{2x_{Na}x_{Cl}} + n_{K-Cl} \ln \frac{x_{K-Cl}}{2x_K x_{Cl}} + n_{Na-K} \ln \frac{x_{Na-K}}{2x_{Na}x_K}\right)$$

(iii) Along NaCl–KCl join

$x_{Na-K} = x_{Na-Na} = x_{K-K} = x_{Cl-Cl} = 0$ $\quad n_{Na-Na} = n_{K-K} = n_{Na-K} = n_{Cl-Cl} = 0$

$x_{NaCl} = x_{Na-Cl}$

$x_{KCl} = x_{K-Cl}$

$n_{Na} = n_{NaCl}$

$n_K = n_{KCl}$

$(n_{Na} + n_K) = n_{Cl}$

$\Delta g_{NaCl} = (g^\circ_{NaCl} - g^\circ_{Na} - g^\circ_{Cl})/2$

$\Delta g_{KCl} = (g^\circ_{KCl} - g^\circ_K - g^\circ_{Cl})/2$

$n_{Na-Cl} = 2n_{Na} = 2n_{NaCl}$

$n_{K-Cl} = 2n_K = 2n_{KCl}$

for n_{Na-Cl} = # of bonds

n_{NaCl} = # of moles of compound

x_{Na-Cl} = bond fraction

x_{NaCl} = component mole fraction

$$x_{Cl} = \frac{1}{2} \qquad x_{Na} = \frac{n_{Na}}{n_{Na} + n_K + n_{Cl}} = (x_{NaCl}/2)$$

$$x_K = (x_{KCl}/2)$$

Substitute into equation (ii):

$$G = (n_{NaCl} g^\circ_{NaCl} + n_{KCl} g^\circ_{KCl})$$

$$+ RT(n_{NaCl} \ln x_{NaCl} + n_{KCl} \ln x_{KCl})$$

$$+ RT(n_{NaCl} + n_{KCl})(-2\ln 2 + 2\ln 2)$$

This is the same as equation (i) only if $Z = 2$!!

2006(II)

Question 5 Along the diagonal: $\begin{cases} y_{Rb} = y_{Cl} = X_{RbCl} \\ y_{Li} = y_F = (1-X_{RbCl}) \end{cases}$

$$g = \left((1-X)^2 g^\circ_{LiF} + X(1-X) g^\circ_{LiCl} + X(1-X)(g^\circ_{RbF}) + X^2 g^\circ_{RbCl}\right)$$
$$+ 2RT\left(X \ln X + (1-X)\ln(1-X)\right) - X^2(1-X)^2\left(\frac{\Delta G^{EX}}{2RT}\right)$$

where $X = X_{RbCl}$

$$\frac{dg}{dX} = -2(1-X) g^\circ_{LiF} + 2X g^\circ_{RbCl} + (1-2X)(g^\circ_{LiCl} + g^\circ_{RbF})$$
$$+ 2RT\left(\ln X - \ln(1-X)\right) - \left[2X(1-X)^2 - 2X^2(1-X)\right]\left(\frac{\Delta G^2}{2RT}\right)$$

$$\frac{d^2g}{dX^2} = 2\overbrace{\left(g^\circ_{LiF} + g^\circ_{RbCl} - g^\circ_{LiCl} - g^\circ_{RbF}\right)}^{\Delta G^{EXCHANGE}} + RT\left(\frac{1}{X} + \frac{1}{1-X}\right)$$
$$- \left(-2X(2)(1-X) + 2(1-X)^2 + 2X^2 - 4X(1-X)\right)\frac{\Delta G}{2RT}$$

$$= 2\Delta G^{EXCH} + 2RT\left(\frac{1}{X} + \frac{1}{1-X}\right) - \left(12X^2 - 12X + 2\right)\frac{(\Delta G^{EXCH})^2}{2RT}$$

By symmetry T_c is at $X = 0.5$

$$2\Delta G^{EX} + 2RT_c + (\Delta G^{EX})^2/2RT_c = 0$$

(i) Ignoring final term

$$2\Delta G^{EX} + 2RT_c = 0 \qquad T_c = \frac{-\Delta G^{EX}}{2R} > 0$$

(ii) With Final term:

$$2RT_c = -2\Delta G^{EX} - (\Delta G^{EX})^2/2RT_c$$

Hence, T_c is lowered by including the final term

2008-II-2

(2) As $X_{CaF_2} \to 0$ $\quad a_{NaCl} \to y_{Na} \cdot y_{Cl}$

= Liquid (Tentative) $\quad NaCl - CaF_2$ $\quad (X_{NaCl} - X_{CaF_2})$

$$y_{Na} = \frac{n_{Na}}{n_{Na}+n_{Ca}} = X_{NaCl}$$

$$y_{Cl} = \frac{n_{Cl}}{n_{Cl}+n_F} = \frac{n_{NaCl}}{n_{NaCl}+2n_{CaF_2}} = \frac{X_{NaCl}}{X_{NaCl}+2X_{CaF_2}} = \left(\frac{X_{NaCl}}{1+X_{CaF_2}}\right)$$

$$a_{NaCl} = X_{NaCl}\left(\frac{X_{NaCl}}{1+X_{CaF_2}}\right)$$

= Solid $\quad$ Each Ca^{2+} ion produces one cation vacancy

$$y_{Na} = \frac{n_{Na}}{n_{Na}+n_{Ca}+n_{Va}} = \frac{n_{NaCl}}{n_{NaCl}+n_{Ca}+n_{Ca}} = \frac{X_{NaCl}}{X_{NaCl}+2X_{CaF_2}}$$

$$y_{Cl} = \frac{n_{Cl}}{n_{Cl}+n_F} = \frac{n_{NaCl}}{n_{NaCl}+2n_{CaF_2}} = \frac{X_{NaCl}}{X_{NaCl}+2X_{CaF_2}} = \frac{X_{NaCl}}{(1+X_{CaF_2})}$$

$$a_{NaCl} = \left(\frac{X_{NaCl}}{(1+X_{CaF_2})}\right)^2$$

2009 – II

(2) (i) $\left.\begin{matrix} n_{NaCl}=1 \\ n_{KCl}=2 \\ n_{KF}=1 \end{matrix}\right\} \Rightarrow \begin{matrix} n_{Na}=1 \\ n_{Cl}=3 \\ n_{K}=3 \\ n_{F}=1 \end{matrix} \Rightarrow \begin{cases} y_{Na}=\frac{n_{Na}}{n_{Na}+n_K}=\frac{1}{4}=(1-y_K) \\ y_K=3/4 \\ y_{Cl}=\frac{n_{Cl}}{n_{Cl}+n_F}=\frac{3}{4}=(1-y_F) \\ y_F=1/4 \end{cases}$

$n_{TOTAL}=(n_{Na}+n_K)=(n_F+n_{Cl})=4$

(ii) $g=(y_{Na}y_{Cl}g^{\circ}_{NaCl}+y_K y_{Cl}g^{\circ}_{KCl}+y_{Na}y_F g^{\circ}_{NaF}+y_K y_F g^{\circ}_{KF}$

$+RT(y_{Na}\ln y_{Na}+y_K\ln y_K)+RT(y_F\ln y_F+y_{Cl}\ln y_{Cl}$

$+[y_{Na}y_K y_{Cl}(-2156)+y_{Na}y_K y_F(2880)+y_F y_{Cl}y_{Na}(2058)$

$+y_F y_{Cl}y_K(38)]$

$-y_{Na}y_K y_F y_{Cl}(\Delta G^{EX^2}/ZRT)$

where: $\Delta G^{EX}=g^{\circ}_{NaCl}+g^{\circ}_{KF}-g^{\circ}_{NaF}-g^{\circ}_{KCl}=20871$

$g=\left[\left(\frac{1}{4}\right)\left(\frac{3}{4}\right)(-556134)+\left(\frac{3}{4}\right)\left(\frac{3}{4}\right)(-596244)+\left(\frac{1}{4}\right)\left(\frac{1}{4}\right)(-683533)\right.$

$\left.+\left(\frac{3}{4}\right)\left(\frac{1}{4}\right)(-702272)\right]$

$+8.315(1271.15)\left(\frac{1}{4}\ln\frac{1}{4}+\frac{3}{4}\ln\frac{3}{4}+\frac{1}{4}\ln\frac{1}{4}+\frac{3}{4}\ln\frac{3}{4}\right)$

$+\left[\left(\frac{1}{4}\right)\left(\frac{3}{4}\right)\left(\frac{3}{4}\right)(-2156)+\left(\frac{1}{4}\right)\left(\frac{3}{4}\right)\left(\frac{1}{4}\right)(2880)+\left(\frac{1}{4}\right)\left(\frac{3}{4}\right)\left(\frac{1}{4}\right)(2058)\right.$

$\left.+\left(\frac{1}{4}\right)\left(\frac{3}{4}\right)\left(\frac{3}{4}\right)(38)\right]$

$-\left(\frac{1}{4}\right)\left(\frac{3}{4}\right)\left(\frac{1}{4}\right)\left(\frac{3}{4}\right)(20871)^2/[6(8.315)(1273.15)]$

$g=-626363\ J/mol$

$G=n_{TOTAL}\cdot g=4(-626363)=-2505452\ \text{Joules}$