Chem 401—Physical Chemistry
Chapter 5 Homework Solutions

Therefore, plot $1/\rho$ against w and extrapolate the tangent to $w = 100$ to obtain V_B/M_B. For the actual procedure, draw up the following table

w	5	10	15	20
$\rho/(\text{g cm}^{-3})$	1.051	1.107	1.167	1.230
$1/(\rho/\text{g cm}^{-3})$	0.951	0.903	0.857	0.813

The values of $1/\rho$ are plotted against w in Figure 5.2.

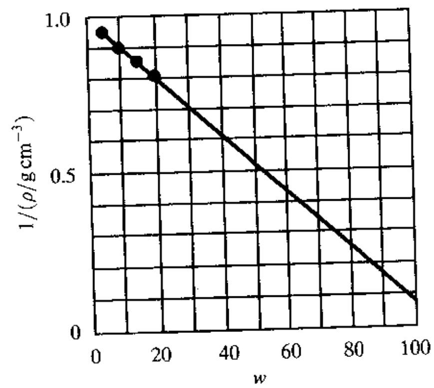

Figure 5.2

Four tangents are drawn to the curve at the four values of w. As the curve is a straight line to within the precision of the data, all four tangents are coincident and all four intercepts are equal at $0.075\ \text{g}^{-1}\ \text{cm}^3$. Thus

$$V(\text{CuSO}_4) = 0.075\ \text{g}^{-1}\ \text{cm}^3 \times 159.6\ \text{g mol}^{-1} = \boxed{12.0\ \text{cm}^3\ \text{mol}^{-1}}$$

P5.6

$$\Delta T = \frac{RT_f^{*2}x_B}{\Delta_{\text{fus}}H}\ [5.36], \quad x_B \approx \frac{n_B}{n(\text{CH}_3\text{COOH})} = \frac{n_B M(\text{CH}_3\text{COOH})}{1000\ \text{g}}$$

Hence, $$\Delta T = \frac{n_B MRT_f^{*2}}{\Delta_{\text{fus}}H \times 1000\ \text{g}} = \frac{b_B MRT_f^{*2}}{\Delta_{\text{fus}}H} \quad [b_B\text{: molality of solution}]$$

$$= b_B \times \left(\frac{(0.06005\ \text{kg mol}^{-1}) \times (8.314\ \text{J K}^{-1}\text{mol}^{-1}) \times (290\ \text{K})^2}{11.4 \times 10^3\ \text{J mol}^{-1}}\right)$$

$$= 3.68\ \text{K} \times b_B/(\text{mol kg}^{-1})$$

Giving for b_B, the apparent molality,

$$b_B = \nu b_B^0 = \frac{\Delta T}{3.68\ \text{K}}\text{mol kg}^{-1}$$

where b_B^0 is the actual molality and ν may be interpreted as the number of ions in solution per one formula unit of KCl. The apparent molar mass of KCl can be determined from the apparent molality by the relation

$$M_B(\text{apparent}) = \frac{b_B^0}{b_B} \times M_B^0 = \frac{1}{\nu} \times M_B^0 = \frac{1}{\nu} \times (74.56\,\text{g mol}^{-1})$$

where M_B^0 is the actual molar mass of KCl.

We can draw up the following table from the data.

$b_B^0/(\text{mol kg}^{-1})$	0.015	0.037	0.077	0.295	0.602
$\Delta T/K$	0.115	0.295	0.470	1.381	2.67
$b_B/(\text{mol kg}^{-1})$	0.0312	0.0802	0.128	0.375	0.726
$\nu = b_B/b_B^0$	2.1	2.2	1.7	1.3	1.2
$M_B(\text{app})/(\text{g mol}^{-1})$	26	34	44	57	62

A possible explanation is that the dissociation of KCl into ions is complete at the lower concentrations but incomplete at the higher concentrations. Values of ν greater than 2 are hard to explain, but they could be a result of the approximations involved in obtaining equation 5.36.

See the original reference for further information about the interpretation of the data.

P5.8 **(a)** On a Raoult's law basis, $a = p/p^*$, $a = \gamma x$, and $\gamma = p/xp^*$. On a Henry's law basis, $a = p/K$, and $\gamma = p/xK$. The vapor pressures of the pure components are given in the table of data and are: $p_I^* = 47.12\,\text{kPa}$, $p_A^* = 37.38\,\text{kPa}$.

(b) The Henry's law constants are determined by plotting the data and extrapolating the low concentration data to $x = 1$. The data are plotted in Figure 5.3. K_A and K_I are estimated as graphical tangents at $x_I = 1$ and $x_I = 0$, respectively. The values obtained are: $K_A = \boxed{60.0\,\text{kPa}}$ and $K_I = \boxed{62.0\,\text{kPa}}$

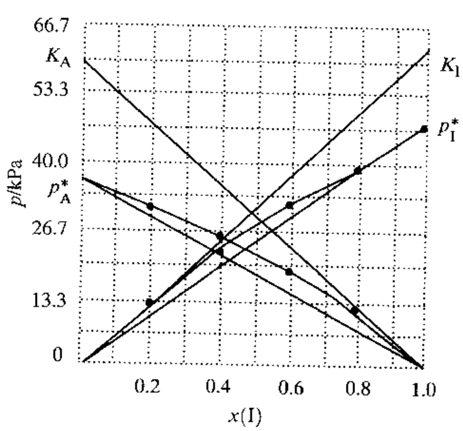

Figure 5.3

Then draw up the following table based on the values of the partial pressures obtained from the plots at the values of x_I given in the figure.

x_I	0	0.2	0.4	0.6	0.8	1.0
p_I/kPa	0	12.3	22.0	30.7	38.7	47.12‡
p_A/kPa	37.38†	30.7	24.7	18.0	10.7	0
$\gamma_I(\mathbf{R})$	—	1.30	1.17	1.09	1.03	1.000$[p_I/x_I p_I^*]$
$\gamma_A(\mathbf{R})$	1.000	1.03	1.10	1.20	1.43	— $[p_A/x_A p_A^*]$
$\gamma_I(\mathbf{H})$	1.000	0.990	0.887	0.824	0.780	0.760$[p_I/x_I K_I^*]$

†The value of p_A^*; ‡the value of p_I^*.

Question. In this problem both I and A were treated as solvents, but only I as a solute. Extend the table by including a row for $\gamma_A(\mathrm{H})$.

P5.10 The partial molar volume of cyclohexane is

$$V_c = \left(\frac{\partial V}{\partial n_c}\right)_{p,T,n_2}$$

A similar expression holds for V_p. V_c can be evaluated graphically by plotting V against n_c and finding the slope at the desired point. In a similar manner, V_p can be evaluated by plotting V against n_p. To find V_c, V is needed at a variety of n_c while holding n_p constant, say at 1.0000 mol; likewise to find V_p, V is needed at a variety of n_p while holding n_c constant. The mole fraction in this system is

$$x_c = \frac{n_c}{n_c + n_p} \quad \text{so } n_c = \frac{x_c n_p}{1 - x_c}$$

From n_c and n_p, the mass of the sample can be calculated, and the volume can be calculated from

$$V = \frac{m}{\rho} = \frac{n_c M_c + n_p M_p}{\rho}$$

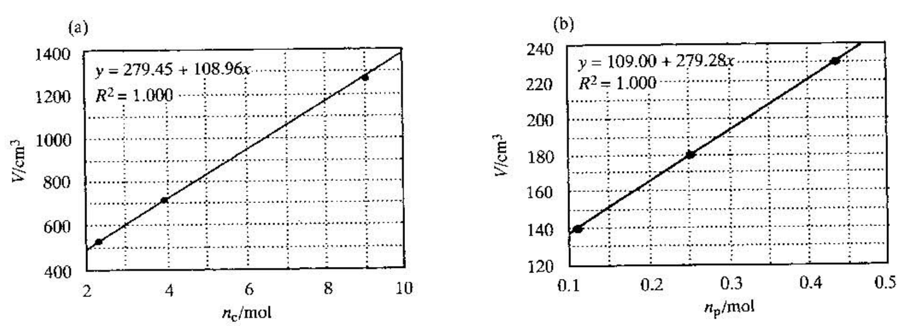

Figure 5.4

The following table is drawn up

n_c/mol($n_p = 1$)	V/cm^3	x_c	ρ/g cm^{-3}	n_p/mol($n_c = 1$)	V/cm^3
2.295	529.4	0.6965	0.7661	0.4358	230.7
3.970	712.2	0.7988	0.7674	0.2519	179.4
9.040	1264	0.9004	0.7697	0.1106	139.9

These values are plotted in Figures 5.4(a) and (b).

These plots show no curvature, so in this case, perhaps due to the limited number of data points, the molar volumes are independent of the mole numbers and are

$$V_c = \boxed{109.0\ \text{cm}^3\ \text{mol}^{-1}} \quad \text{and} \quad V_p = \boxed{279.3\ \text{cm}^3\ \text{mol}^{-1}}$$

P5.12 The activity of a solvent is

$$a_A = \frac{p_A}{p_A^*} = x_A\gamma_A$$

so the activity coefficient is

$$\gamma_A = \frac{p_A}{x_A p_A^*} = \frac{y_A p}{x_A p_A^*}$$

where the last equality applies Dalton's law of partial pressures to the vapor phase.

Substituting the data, the following table of results is obtained.

p/kPa	x_T	y_T	γ_T	γ_E
23.40	0.000	0.000		
21.75	0.129	0.065	0.418	0.998
20.25	0.228	0.145	0.490	1.031
18.75	0.353	0.285	0.576	1.023
18.15	0.511	0.535	0.723	0.920
20.25	0.700	0.805	0.885	0.725
22.50	0.810	0.915	0.966	0.497
26.30	1.000	1.000		

P5.14 $S = S_0 e^{\tau/T}$ may be written in the form $\ln S = \ln S_0 + (\tau/T)$, which indicates that a plot of $\ln S$ against $1/T$ should be linear with slope τ and intercept $\ln S_0$. Linear regression analysis gives $\boxed{\tau = 165\ \text{K}}$, standard deviation = 2 K

$$\ln(S_0/\text{mol dm}^{-3}) = 2.990,\ \text{standard deviation} = 0.007; S_0 = e^{2.990}\text{mol dm}^{-3} = \boxed{19.89\ \text{mol dm}^{-3}}$$

$$R = \boxed{0.99978}$$

The linear regression explains 99.98 percent of the variation.

At this composition

$$V_E = 56.0\,\text{cm}^3\text{mol}^{-1}, \qquad V_W = 17.5\,\text{cm}^3\,\text{mol}^{-1} \text{ [Fig.5.1 of the text].}$$

$$\text{Therefore, } n_E = \frac{100\,\text{cm}^3}{(56.0\,\text{cm}^3\,\text{mol}^{-1}) + (2.557) \times (17.5\,\text{cm}^3\,\text{mol}^{-1})} = 0.993\,\text{mol},$$

$$n_W = (2.557) \times (0.993\,\text{mol}) = 2.54\,\text{mol}.$$

The fact that these amounts correspond to a mixture containing 50 per cent by mass of both components is easily checked as follows:

$$m_E = n_E M_E = (0.993\,\text{mol}) \times (46.07\,\text{g mol}^{-1}) = 45.7\,\text{g ethanol},$$

$$m_W = n_W M_W = (2.54\,\text{mol}) \times (18.02\,\text{g mol}^{-1}) = 45.7\,\text{g water}.$$

At 20°C the densities of ethanol and water are,

$$\rho_E = 0.789\,\text{g cm}^{-3}, \quad \rho_W = 0.997\,\text{g cm}^{-3}. \text{ Hence,}$$

$$V_E = \frac{m_E}{\rho_E} = \frac{45.7\,\text{g}}{0.789\,\text{g cm}^{-3}} = \boxed{57.9\,\text{cm}^3} \text{ of ethanol,}$$

$$V_W = \frac{m_W}{\rho_W} = \frac{45.7\,\text{g}}{0.997\,\text{g cm}^{-3}} = \boxed{45.8\,\text{cm}^3} \text{ of water.}$$

The change in volume upon adding a small amount of ethanol can be approximated by

$$\Delta V = \int \mathrm{d}V \approx \int V_E \mathrm{d}n_E \approx V_E \Delta n_E$$

where we have assumed that both V_E and V_W are constant over this small range of n_E. Hence

$$\Delta V \approx (56.0\,\text{cm}^3\text{mol}^{-1}) \times \left(\frac{(1.00\,\text{cm}^3) \times (0.789\,\text{g cm}^{-3})}{(46.07\,\text{g mol}^{-1})}\right) = \boxed{+0.96\,\text{cm}^3}.$$

P5.7

$$b_B = \frac{\Delta T}{K_f} = \frac{0.0703\,\text{K}}{1.86\,\text{K}/(\text{mol kg}^{-1})} = 0.0378\,\text{mol kg}^{-1}.$$

Since the solution molality is nominally $0.0096\,\text{mol kg}^{-1}$ in $Th(NO_3)_4$, each formula unit supplies $\frac{0.0378}{0.0096} \approx \boxed{4 \text{ ions}}$. (More careful data, as described in the original reference gives $\nu \approx 5$ to 6.)

P5.9 The data are plotted in Figure 5.3. The regions where the vapor pressure curves show approximate straight lines are denoted R for Raoult and H for Henry. A and B denote acetic acid and benzene respectively.

As in Problem 5.8, we need to form $\gamma_A = \frac{p_A}{x_A p_A^*}$ and $\gamma_B = \frac{p_B}{x_B p_B^*}$ for the Raoult's law activity coefficients and $\gamma_B = \frac{p_B}{x_B K}$ for the activity coefficient of benzene on a Henry's law basis, with K determined by extrapolation. We use $p^*{}_A = 7.3$ kPa, $p_B^* = 35.2$ kPa, and $K^*{}_B = 80.0$ kPa to draw up the following table.

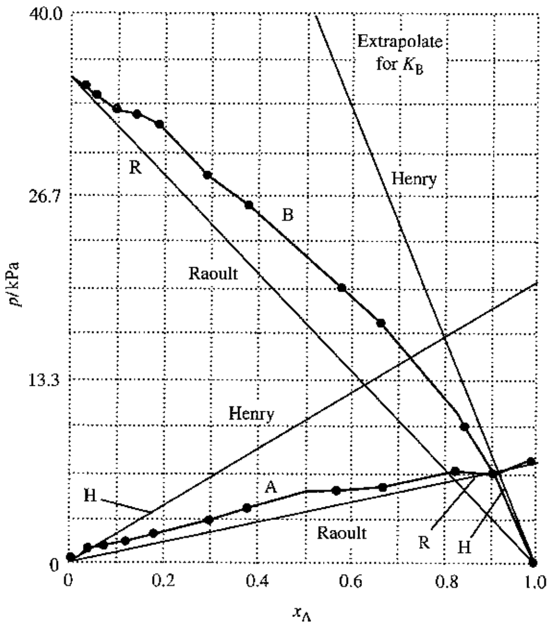

Figure 5.3

x_A	0	0.2	0.4	0.6	0.8	1.0
p_A/kPa	0	2.7	4.0	5.1	6.7	7.3
p_B/kPa	35.2	30.4	25.3	20.0	12.4	0
a_A(R)	0	0.36	0.55	0.69	0.91	1.00[p_A/p_A^*]
a_B(R)	1.00	0.86	0.72	0.57	0.35	0[p_B/p_B^*]
γ_A(R)	—	1.82	1.36	1.15	1.14	1.00[$p_A/x_Ap_A^*$]
γ_B(R)	1.00	1.08	1.20	1.42	1.76	—[$p_B/x_Bp_B^*$]
a_B(H)	0.44	0.38	0.32	0.25	0.16	0[p_B/K_B]
γ_B(H)	0.44	0.48	0.53	0.63	0.78	1.00[p_B/x_BK_B]

G^E is defined as [Section 5.4]

$$G^E = \Delta_{mix}G(\text{actual}) - \Delta_{mix}G(\text{ideal}) = nRT(x_A \ln a_A + x_B \ln a_B) - nRT(x_A \ln x_A + x_B \ln x_B)$$

and, with $a = \gamma x$,

$$G^E = nRT(x_A \ln \gamma_A + x_A \ln \gamma_B).$$

For $n = 1$, we can draw up the following table from the information above and $RT = 2.69\,\text{kJ mol}^{-1}$.

x_A	0	0.2	0.4	0.6	0.8	1.0
$x_A \ln \gamma_A$	0	0.12	0.12	0.08	0.10	0
$x_B \ln \gamma_B$	0	0.06	0.11	0.14	0.11	0
$G^E/(\text{kJ mol}^{-1})$	0	0.48	0.62	0.59	0.56	0

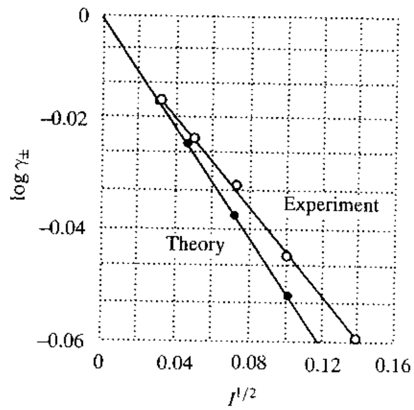

Figure 5.5

Solutions to theoretical problems

P5.18 $x_A\,d\mu_A + x_B\,d\mu_B = 0$ [5.12, Gibbs–Duhem equation]

Therefore, after dividing through by dx_A

$$x_A\left(\frac{\partial\mu_A}{\partial x_A}\right)_{p,T} + x_B\left(\frac{\partial\mu_B}{\partial x_A}\right)_{p,T} = 0$$

or, since $dx_B = -dx_A$, as $x_A + x_B = 1$

$$x_A\left(\frac{\partial\mu_A}{\partial x_A}\right)_{p,T} - x_B\left(\frac{\partial\mu_B}{\partial x_B}\right)_{p,T} = 0$$

or, $\left(\frac{\partial\mu_A}{\partial \ln x_A}\right)_{p,T} = \left(\frac{\partial\mu_B}{\partial \ln x_B}\right)_{p,T}$ $\left[d\ln x = \frac{dx}{x}\right]$

Then, since $\mu = \mu^{\ominus} + RT\ln\frac{f}{p^{\ominus}}$, $\left(\frac{\partial \ln f_A}{\partial \ln x_A}\right)_{p,T} = \left(\frac{\partial \ln f_B}{\partial \ln x_B}\right)_{p,T}$

On replacing f by p, $\left(\frac{\partial \ln p_A}{\partial \ln x_A}\right)_{p,T} = \left(\frac{\partial \ln p_B}{\partial \ln x_B}\right)_{p,T}$

If A satisfies Raoult's law, we can write $p_A = x_A p_A^*$, which implies that

$$\left(\frac{\partial \ln p_A}{\partial \ln x_A}\right)_{p,T} = \frac{\partial \ln x_A}{\partial \ln x_A} + \frac{\partial \ln p_A^*}{\partial \ln x_A} = 1 + 0$$

Therefore, $\left(\frac{\partial \ln p_B}{\partial \ln x_B}\right)_{p,T} = 1$

which is satisfied if $p_B = x_B p_B$ (by integration, or inspection). Hence, if A satisfies Raoult's law, so does B.