# CHAPTER 5  Simple mixtures

## TOPIC 5A  The thermodynamic description of mixtures

### Discussion questions

**5A.1** Explain the concept of partial molar quantity, and justify the remark that the partial molar property of a solute depends on the properties of the solvent too.

**5A.2** Explain how thermodynamics relates non-expansion work to a change in composition of a system.

**5A.3** Are there any circumstances under which two (real) gases will not mix spontaneously?

**5A.4** Explain how Raoult's law and Henry's law are used to specify the chemical potential of a component of a mixture.

**5A.5** Explain the molecular origin of Raoult's law and Henry's law.

### Exercises

**5A.1(a)** A polynomial fit to measurements of the total volume of a binary mixture of A and B is

$$v = 987.93 + 35.6774x - 0.45923x^2 + 0.017325x$$

where $v = V/cm^3$, $x = n_B/mol$, and $n_B$ is the amount of B present. Determine the partial molar volumes of A and B.

**5A.1(b)** A polynomial fit to measurements of the total volume of a binary mixture of A and B is

$$v = 778.55 - 22.5749x + 0.56892x^2 + 0.01023x^3 + 0.00234x$$

where $v = V/cm^3$, $x = n_B/mol$, and $n_B$ is the amount of B present. Determine the partial molar volumes of A and B.

**5A.2(a)** The volume of an aqueous solution of NaCl at 25 °C was measured at a series of molalities $b$, and it was found that the volume fitted the expression $v = 1003 + 16.62x + 1.77x^{3/2} + 0.12x^2$ where $v = V/cm^3$, $V$ is the volume of a solution formed from 1.000 kg of water and $x = b/b^\ominus$. Calculate the partial molar volume of the components in a solution of molality 0.100 mol kg$^{-1}$.

**5A.2(b)** At 18 °C the total volume $V$ of a solution formed from MgSO$_4$ and 1.000 kg of water fits the expression $v = 1001.21 + 34.69(x - 0.070)^2$, where $v = V/cm^3$ and $x = b/bx = b/b^\ominus$. Calculate the partial molar volumes of the salt and the solvent when in a solution of molality 0.050 mol kg$^{-1}$.

**5A.3(a)** Suppose that $n_A = 0.10n_B$ and a small change in composition results in $\mu_A$ changing by $\delta\mu_A = +12$ J mol$^{-1}$, by how much will $\mu_B$ change?

**5A.3(b)** Suppose that $n_A = 0.22n_B$ and a small change in composition results in $\mu_A$ changing by $\delta\mu_A = -15$ J mol$^{-1}$, by how much will $\mu_B$ change?

**5A.4(a)** Consider a container of volume 5.0 dm$^3$ that is divided into two compartments of equal size. In the left compartment there is nitrogen at 1.0 atm and 25 °C; in the right compartment there is hydrogen at the same temperature and pressure. Calculate the entropy and Gibbs energy of mixing when the partition is removed. Assume that the gases are perfect.

**5A.4(b)** Consider a container of volume 250 cm$^3$ that is divided into two compartments of equal size. In the left compartment there is argon at 100 kPa and 0 °C; in the right compartment there is neon at the same temperature and pressure. Calculate the entropy and Gibbs energy of mixing when the partition is removed. Assume that the gases are perfect.

**5A.5(a)** Air is a mixture with mass percentage composition 75.5 (N$_2$), 23.2 (O$_2$), 1.3 (Ar). Calculate the entropy of mixing when it is prepared from the pure (and perfect) gases.

**5A.5(b)** When carbon dioxide is taken into account, the mass percentage composition of air is 75.52 (N$_2$), 23.15 (O$_2$), 1.28 (Ar), and 0.046 (CO$_2$). What is the change in entropy from the value in the preceding exercise?

**5A.6(a)** The vapour pressure of benzene at 20 °C is 10 kPa and that of methylbenzene is 2.8 kPa at the same temperature. What is the vapour pressure of a mixture of equal masses of each component?

**5A.6(b)** At 90 °C the vapour pressure of 1,2-dimethylbenzene is 20 kPa and that of 1,3-dimethylbenzene is 18 kPa. What is the composition of the vapour of an equimolar mixture of the two components?

**5A.7(a)** The partial molar volumes of acetone (propanone) and chloroform (trichloromethane) in a mixture in which the mole fraction of CHCl$_3$ is 0.4693 are 74.166 cm$^3$ mol$^{-1}$ and 80.235 cm$^3$ mol$^{-1}$, respectively. What is the volume of a solution of mass 1.000 kg?

**5A.7(b)** The partial molar volumes of two liquids A and B in a mixture in which the mole fraction of A is 0.3713 are 188.2 cm$^3$ mol$^{-1}$ and 176.14 cm$^3$ mol$^{-1}$, respectively. The molar masses of the A and B are 241.1 g mol$^{-1}$ and 198.2 g mol$^{-1}$. What is the volume of a solution of mass 1.000 kg?

**5A.8(a)** At 25 °C, the density of a 50 per cent by mass ethanol–water solution is 0.914 g cm$^{-3}$. Given that the partial molar volume of water in the solution is 17.4 cm$^3$ mol$^{-1}$, calculate the partial molar volume of the ethanol.

**5A.8(b)** At 20 °C, the density of a 20 per cent by mass ethanol/water solution is 968.7 kg m$^{-3}$. Given that the partial molar volume of ethanol in the solution is 52.2 cm$^3$ mol$^{-1}$, calculate the partial molar volume of the water.

**5A.9(a)** At 300 K, the partial vapour pressure of HCl (that is, the partial pressure of the HCl vapour) in liquid GeCl$_4$ is as follows:

| $x_{HCl}$ | 0.005 | 0.012 | 0.019 |
|---|---|---|---|
| $p_{HCl}$/kPa | 32.0 | 76.9 | 121.8 |

Show that the solution obeys Henry's law in this range of mole fractions, and calculate Henry's law constant at 300 K.

**5A.9(b)** At 310 K, the partial vapour pressure of a substance B dissolved in a liquid A is as follows:

| $x_B$ | 0.010 | 0.015 | 0.020 |
|---|---|---|---|
| $p_B$/kPa | 82.0 | 122.0 | 166.1 |

Show that the solution obeys Henry's law in this range of mole fractions, and calculate Henry's law constant at 310 K.

**5A.10(a)** Calculate the molar solubility of nitrogen in benzene exposed to air at 25 °C; partial pressures were calculated in *Example* 1A.3 of Topic 1A.
**5A.10(b)** Calculate the molar solubility of methane at 1.0 bar in benzene at 25 °C.

**5A.11(a)** Use Henry's law and the data in Table 5A.1 to calculate the solubility (as a molality) of $CO_2$ in water at 25 °C when its partial pressure is (i) 0.10 atm, (ii) 1.00 atm.
**5A.11(b)** The mole fractions of $N_2$ and $O_2$ in air at sea level are approximately 0.78 and 0.21. Calculate the molalities of the solution formed in an open flask of water at 25 °C.

**5A.12(a)** A water carbonating plant is available for use in the home and operates by providing carbon dioxide at 5.0 atm. Estimate the molar concentration of the soda water it produces.
**5A.12(b)** After some weeks of use, the pressure in the water carbonating plant mentioned in the previous exercise has fallen to 2.0 atm. Estimate the molar concentration of the soda water it produces at this stage.

## Problems

**5A.1** The experimental values of the partial molar volume of a salt in water are found to fit the expression $v_B = 5.117 + 19.121x^{1/2}$, where $v_B = V_B/(\text{cm}^3\,\text{mol}^{-1})$ and $x$ is the numerical value of the molality of B $(x = b/b^{\ominus})$. Use the Gibbs–Duhem equation to derive an equation for the molar volume of water in the solution. The molar volume of pure water at the same temperature is 18.079 $\text{cm}^3\,\text{mol}^{-1}$.

**5A.2** The compound *p*-azoxyanisole forms a liquid crystal. 5.0 g of the solid was placed in a tube, which was then evacuated and sealed. Use the phase rule to prove that the solid will melt at a definite temperature and that the liquid crystal phase will make a transition to a normal liquid phase at a definite temperature.

**5A.3** The following table gives the mole fraction of methylbenzene (A) in liquid and gaseous mixtures ($x_A$ and $y_A$, respectively) with butanone at equilibrium at 303.15 K and the total pressure $p$. Take the vapour to be perfect and calculate the partial pressures of the two components. Plot them against their respective mole fractions in the liquid mixture and find the Henry's law constants for the two components.

| $x_A$ | 0 | 0.0898 | 0.2476 | 0.3577 | 0.5194 | 0.6036 |
|---|---|---|---|---|---|---|
| $y_A$ | 0 | 0.0410 | 0.1154 | 0.1762 | 0.2772 | 0.3393 |
| $p$/kPa | 36.066 | 34.121 | 30.900 | 28.626 | 25.239 | 23.402 |

| $x_A$ | 0.7188 | 0.8019 | 0.9105 | 1 |
|---|---|---|---|---|
| $y_A$ | 0.4450 | 0.5435 | 0.7284 | 1 |
| $p$/kPa | 20.6984 | 18.592 | 15.496 | 12.295 |

**5A.4** The densities of aqueous solutions of copper(II) sulfate at 20 °C were measured as set out below. Determine and plot the partial molar volume of $CuSO_4$ in the range of the measurements.

| $m(CuSO_4)$/g | 5 | 10 | 15 | 20 |
|---|---|---|---|---|
| $\rho$/(g cm$^{-3}$) | 1.051 | 1.107 | 1.167 | 1.230 |

where $m(CuSO_4)$ is the mass of $CuSO_4$ dissolved in 100 g of solution.

**5A.5** Haemoglobin, the red blood protein responsible for oxygen transport, binds about 1.34 $\text{cm}^3$ of oxygen per gram. Normal blood has a haemoglobin concentration of 150 g dm$^{-3}$. Haemoglobin in the lungs is about 97 per cent saturated with oxygen, but in the capillary is only about 75 per cent saturated. What volume of oxygen is given up by 100 $\text{cm}^3$ of blood flowing from the lungs in the capillary?

**5A.6** Use the data from *Example* 5A.1 to determine the value of $b$ at which $V_E$ has a minimum value.

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# TOPIC 5B   The properties of solutions

## Discussion questions

**5B.1** Explain what is meant by a regular solution; what additional features distinguish a real solution from a regular solution?

**5B.2** Explain the physical origin of colligative properties.

**5B.3** Colligative properties are independent of the identity of the solute. Why, then, can osmometry be used to determine the molar mass of a solute?

## Exercises

**5B.1(a)** Predict the partial vapour pressure of HCl above its solution in liquid germanium tetrachloride of molality 0.10 mol kg$^{-1}$. For data, see Exercise 5A.10(a).
**5B.1(b)** Predict the partial vapour pressure of the component B above its solution in A in Exercise 5A.10(b) when the molality of B is 0.25 mol kg$^{-1}$. The molar mass of A is 74.1 g mol$^{-1}$.

**5B.2(a)** The vapour pressure of benzene is 53.3 kPa at 60.6 °C, but it fell to 51.5 kPa when 19.0 g of a non-volatile organic compound was dissolved in 500 g of benzene. Calculate the molar mass of the compound.

**5B.2(b)** The vapour pressure of 2-propanol is 50.00 kPa at 338.8 K, but it fell to 49.62 kPa when 8.69 g of a non-volatile organic compound was dissolved in 250 g of 2-propanol. Calculate the molar mass of the compound.

**5B.3(a)** The addition of 100 g of a compound to 750 g of $CCl_4$ lowered the freezing point of the solvent by 10.5 K. Calculate the molar mass of the compound.
**5B.3(b)** The addition of 5.00 g of a compound to 250 g of naphthalene lowered the freezing point of the solvent by 0.780 K. Calculate the molar mass of the compound.

**5B.4(a)** The osmotic pressure of an aqueous solution at 300 K is 120 kPa. Calculate the freezing point of the solution.
**5B.4(b)** The osmotic pressure of an aqueous solution at 288 K is 99.0 kPa. Calculate the freezing point of the solution.

**5B.5(a)** Calculate the Gibbs energy, entropy, and enthalpy of mixing when 0.50 mol $C_6H_{14}$ (hexane) is mixed with 2.00 mol $C_7H_{16}$ (heptane) at 298 K; treat the solution as ideal.
**5B.5(b)** Calculate the Gibbs energy, entropy, and enthalpy of mixing when 1.00 mol $C_6H_{14}$ (hexane) is mixed with 1.00 mol $C_7H_{16}$ (heptane) at 298 K; treat the solution as ideal.

**5B.6(a)** What proportions of hexane and heptane should be mixed (i) by mole fraction, (ii) by mass in order to achieve the greatest entropy of mixing?
**5B.6(b)** What proportions of benzene and ethylbenzene should be mixed (i) by mole fraction, (ii) by mass in order to achieve the greatest entropy of mixing?

**5B.7(a)** The enthalpy of fusion of anthracene is 28.8 kJ mol$^{-1}$ and its melting point is 217 °C. Calculate its ideal solubility in benzene at 25 °C.
**5B.7(b)** Predict the ideal solubility of lead in bismuth at 280 °C given that its melting point is 327 °C and its enthalpy of fusion is 5.2 kJ mol$^{-1}$.

**5B.8(a)** The osmotic pressure of solutions of polystyrene in toluene were measured at 25 °C and the pressure was expressed in terms of the height of the solvent of density 1.004 g cm$^{-3}$:

| $c/(\text{g dm}^{-3})$ | 2.042 | 6.613 | 9.521 | 12.602 |
|---|---|---|---|---|
| $h/\text{cm}$ | 0.592 | 1.910 | 2.750 | 3.600 |

Calculate the molar mass of the polymer.

**5B.8(b)** The molar mass of an enzyme was determined by dissolving it in water, measuring the osmotic pressure at 20 °C, and extrapolating the data to zero concentration. The following data were obtained:

| $c/(\text{mg cm}^{-3})$ | 3.221 | 4.618 | 5.112 | 6.722 |
|---|---|---|---|---|
| $h/\text{cm}$ | 5.746 | 8.238 | 9.119 | 11.990 |

Calculate the molar mass of the enzyme.

**5B.9(a)** A dilute solution of bromine in carbon tetrachloride behaves as an ideal dilute solution. The vapour pressure of pure $CCl_4$ is 33.85 Torr at 298 K. The Henry's law constant when the concentration of $Br_2$ is expressed as a mole fraction is 122.36 Torr. Calculate the vapour pressure of each component, the total pressure, and the composition of the vapour phase when the mole fraction of $Br_2$ is 0.050, on the assumption that the conditions of the ideal dilute solution are satisfied at this concentration.

**5B.9(b)** The vapour pressure of a pure liquid A is 23 kPa at 20 °C and its Henry's law constant in liquid B is 73 kPa. Calculate the vapour pressure of each component, the total pressure, and the composition of the vapour phase when the mole fraction of A is 0.066 on the assumption that the conditions of the ideal dilute solution are satisfied at this concentration.

**5B.10(a)** At 90 °C, the vapour pressure of methylbenzene is 53.3 kPa and that of 1,2-dimethylbenzene is 20.0 kPa. What is the composition of a liquid mixture that boils at 90 °C when the pressure is 0.50 atm? What is the composition of the vapour produced?
**5B.10(b)** At 90 °C, the vapour pressure of 1,2-dimethylbenzene is 20 kPa and that of 1,3-dimethylbenzene is 18 kPa What is the composition of a liquid mixture that boils at 90 °C when the pressure is 19 kPa? What is the composition of the vapour produced?

**5B.11(a)** The vapour pressure of pure liquid A at 300 K is 76.7 kPa and that of pure liquid B is 52.0 kPa. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.350. Calculate the total pressure of the vapour and the composition of the liquid mixture.
**5B.11(b)** The vapour pressure of pure liquid A at 293 K is 68.8 kPa and that of pure liquid B is 82.1 kPa. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.612. Calculate the total pressure of the vapour and the composition of the liquid mixture.

**5B.12(a)** It is found that the boiling point of a binary solution of A and B with $x_A = 0.6589$ is 88 °C. At this temperature the vapour pressures of pure A and B are 127.6 kPa and 50.60 kPa, respectively. (i) Is this solution ideal? (ii) What is the initial composition of the vapour above the solution?
**5B.12(b)** It is found that the boiling point of a binary solution of A and B with $x_A = 0.4217$ is 96 °C. At this temperature the vapour pressures of pure A and B are 110.1 kPa and 76.5 kPa, respectively. (i) Is this solution ideal? (ii) What is the initial composition of the vapour above the solution?

**5B.13(a)** Dibromoethene (DE, $p_{DE}^* = 22.9$ kPa at 358 K) and dibromopropene (DP, $p_{DP}^* = 17.1$ kPa at 358 K) form a nearly ideal solution. If $x_{DE} = 0.60$, what is (i) $p_{total}$ when the system is all liquid, (ii) the composition of the vapour when the system is still almost all liquid.
**5B.13(b)** Benzene and toluene form nearly ideal solutions. Consider an equimolar solution of benzene and toluene. At 20 °C the vapour pressures of pure benzene and toluene are 9.9 kPa and 2.9 kPa, respectively. The solution is boiled by reducing the external pressure below the vapour pressure. Calculate (i) the pressure when boiling begins, (ii) the composition of each component in the vapour, and (iii) the vapour pressure when only a few drops of liquid remain. Assume that the rate of vaporization is low enough for the temperature to remain constant at 20 °C.

## Problems

**5B.1** Potassium fluoride is very soluble in glacial acetic acid and the solutions have a number of unusual properties. In an attempt to understand them, freezing point depression data were obtained by taking a solution of known molality and then diluting it several times (J. Emsley, *J. Chem. Soc. A*, 2702 (1971)). The following data were obtained:

| $b/(\text{mol kg}^{-1})$ | 0.015 | 0.037 | 0.077 | 0.295 | 0.602 |
|---|---|---|---|---|---|
| $\Delta T/\text{K}$ | 0.115 | 0.295 | 0.470 | 1.381 | 2.67 |

Calculate the apparent molar mass of the solute and suggest an interpretation. Use $\Delta_{fus}H = 11.4$ kJ mol$^{-1}$ and $T_f^* = 290$ K.

**5B.2** In a study of the properties of an aqueous solution of $Th(NO_3)_4$ (by A. Apelblat, D. Azoulay, and A. Sahar, *J. Chem. Soc. Faraday Trans., I*, 1618 (1973)), a freezing point depression of 0.0703 K was observed for an aqueous solution of molality 9.6 mmol kg$^{-1}$. What is the apparent number of ions per formula unit?

**5B.3**[‡] Aminabhavi et al. examined mixtures of cyclohexane with various long-chain alkanes (T.M. Aminabhavi et al., *J. Chem. Eng. Data* **41**, 526 (1996)). Among their data are the following measurements of the density of a mixture of cyclohexane and pentadecane as a function of mole fraction of cyclohexane ($x_c$) at 298.15 K:

| $x_c$ | 0.6965 | 0.7988 | 0.9004 |
|---|---|---|---|
| $\rho/(\text{g cm}^{-3})$ | 0.7661 | 0.7674 | 0.7697 |

Compute the partial molar volume for each component in a mixture which has a mole fraction of cyclohexane of 0.7988.

**5B.4**[‡] Comelli and Francesconi examined mixtures of propionic acid with various other organic liquids at 313.15 K (F. Comelli and R. Francesconi, *J. Chem. Eng. Data* **41**,101 (1996)). They report the excess volume of mixing

[‡] These problems were provided by Charles Trapp and Carmen Giunta.

propionic acid with oxane as $V^E = x_1x_2\{a_0 + a_1(x_1 - x_2)\}$, where $x_1$ is the mole fraction of propionic acid, $x_2$ that of oxane, $a_0 = -2.4697\,\text{cm}^3\,\text{mol}^{-1}$ and $a_1 = 0.0608\,\text{cm}^3\,\text{mol}^{-1}$. The density of propionic acid at this temperature is $0.97174\,\text{g cm}^{-3}$; that of oxane is $0.86398\,\text{g cm}^{-3}$. (a) Derive an expression for the partial molar volume of each component at this temperature. (b) Compute the partial molar volume for each component in an equimolar mixture.

**5B.5‡** Equation 5B.15 indicates, after it has been converted into an expression for $x_B$, that solubility is an exponential function of temperature. The data in the table below gives the solubility, $S$, of calcium acetate in water as a function of temperature.

| $\theta/°C$ | 0 | 20 | 40 | 60 | 80 |
|---|---|---|---|---|---|
| $S/(\text{g }(100\text{ g solvent})^{-1})$ | 36.4 | 34.9 | 33.7 | 32.7 | 31.7 |

Determine the extent to which the data fit the exponential $S = S_0 e^{\tau/T}$ and obtain values for $S_0$ and $\tau$. Express these constants in terms of properties of the solute.

**5B.6** The excess Gibbs energy of solutions of methylcyclohexane (MCH) and tetrahydrofuran (THF) at 303.15 K were found to fit the expression

$$G^E = RTx(1-x)\left\{0.4857 - 0.1077(2x-1) + 0.0191(2x-1)^2\right\}$$

where $x$ is the mole fraction of the methylcyclohexane. Calculate the Gibbs energy of mixing when a mixture of 1.00 mol of MCH and 3.00 mol of THF is prepared.

**5B.7‡** Figure 5.1 shows $\Delta_{\text{mix}}G(x_{Pb},T)$ for a mixture of copper and lead. (a) What does the graph reveal about the miscibility of copper and lead and the spontaneity of solution formation? What is the variance ($F$) at (i) 1500 K, (ii) 1100 K? (b) Suppose that at 1500 K a mixture of composition (i) $x_{Pb} = 0.1$, (ii) $x_{Pb} = 0.7$, is slowly cooled to 1100 K. What is the equilibrium composition of the final mixture? Include an estimate of the relative amounts of each phase. (c) What is the solubility of (i) lead in copper, (ii) copper in lead at 1100 K?
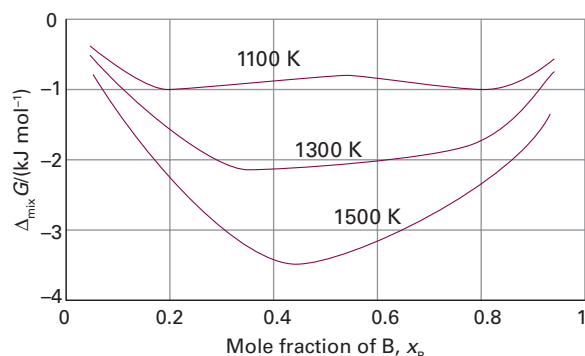


**Figure 5.1** The Gibbs energy of mixing of copper and lead.

**5B.8** The excess Gibbs energy of a certain binary mixture is equal to $gRTx(1-x)$ where $g$ is a constant and $x$ is the mole fraction of a solute A. Find an expression for the chemical potential of A in the mixture and sketch its dependence on the composition.

**5B.9** Use the Gibbs–Helmholtz equation to find an expression for $d \ln x_A$ in terms of $dT$. Integrate $d \ln x_A$ from $x_A = 0$ to the value of interest, and

integrate the right-hand side from the transition temperature for the pure liquid A to the value in the solution. Show that, if the enthalpy of transition is constant, then eqns 5B.9 and 5B.12 are obtained.

**5B.10‡** Polymer scientists often report their data in a variety of units. For example, in the determination of molar masses of polymers in solution by osmometry, osmotic pressures are often reported in grams per square centimetre ($\text{g cm}^{-2}$) and concentrations in grams per cubic centimetre ($\text{g cm}^{-3}$). (a) With these choices of units, what would be the units of $R$ in the van 't Hoff equation? (b) The data in the table below on the concentration dependence of the osmotic pressure of polyisobutene in chlorobenzene at 25 °C have been adapted from J. Leonard and H. Daoust (*J. Polymer Sci.* **57**, 53 (1962)). From these data, determine the molar mass of polyisobutene by plotting $\Pi/c$ against $c$. (c) 'Theta solvents' are solvents for which the second osmotic coefficient is zero; for 'poor' solvents the plot is linear and for good solvents the plot is nonlinear. From your plot, how would you classify chlorobenzene as a solvent for polyisobutene? Rationalize the result in terms of the molecular structure of the polymer and solvent. (d) Determine the second and third osmotic virial coefficients by fitting the curve to the virial form of the osmotic pressure equation. (e) Experimentally, it is often found that the virial expansion can be represented as

$$\Pi/c = RT/M(1 + B_c' + gB'^2c^2 + \ldots)$$

and in good solvents, the parameter $g$ is often about 0.25. With terms beyond the second power ignored, obtain an equation for $(\Pi/c)^{1/2}$ and plot this quantity against $c$. Determine the second and third virial coefficients from the plot and compare to the values from the first plot. Does this plot confirm the assumed value of $g$?

| $10^{-2}(\Pi/c)/(\text{g cm}^{-2}/\text{g cm}^{-3})$ | 2.6 | 2.9 | 3.6 | 4.3 | 6.0 | 12.0 |
|---|---|---|---|---|---|---|
| $c/(\text{g cm}^{-3})$ | 0.0050 | 0.010 | 0.020 | 0.033 | 0.057 | 0.10 |

| $10^{-2}(\Pi/c/(\text{g cm}^{-2}//\text{g cm}^{-3})$ | 19.0 | 31.0 | 38.0 | 52 | 63 |
|---|---|---|---|---|---|
| $c/(\text{g cm}^{-3})$ | 0.145 | 0.195 | 0.245 | 0.27 | 0.29 |

**5B.11‡** K. Sato, F.R. Eirich, and J.E. Mark (*J. Polymer Sci., Polym. Phys.* **14**, 619 (1976)) have reported the data in the table below for the osmotic pressures of polychloroprene ($\rho = 1.25\,\text{g cm}^{-3}$) in toluene ($\rho = 0.858\,\text{g cm}^{-3}$) at 30 °C. Determine the molar mass of polychloroprene and its second osmotic virial coefficient.

| $c/(\text{mg cm}^{-3})$ | 1.33 | 2.10 | 4.52 | 7.18 | 9.87 |
|---|---|---|---|---|---|
| $\Pi/(\text{N m}^{-2})$ | 30 | 51 | 132 | 246 | 390 |

**5B.12** Use mathematical software, a spreadsheet, or the *Living graphs* on the web site for this book to draw graphs of $\Delta_{\text{mix}}G$ against $x_A$ at different temperatures in the range 298 K to 500 K. For what value of $x_A$ does $\Delta_{\text{mix}}G$ depend on temperature most strongly?

**5B.13** Using the graph in Fig. 5B.4, fix $\xi$ and vary the temperature. For what value of $x_A$ does the excess enthalpy depend on temperature most strongly?

**5B.14** Derive an expression for the temperature coefficient of the solubility, $dx_B/dT$, and plot it as a function of temperature for several values of the enthalpy of fusion.

**5B.15** Calculate the osmotic virial coefficient $B$ from the data in *Example* 5B.2.

# TOPIC 5C   Phase diagrams of binary systems

## Discussion questions

**5C.1** Draw phase diagrams for the following types of systems. Label the regions of the diagrams, stating what materials (possibly compounds or azeotropes) are present and whether they are solid liquid or gas:

(a) two-component, temperature–composition, solid–liquid diagram, one compound AB formed that melts congruently, negligible solid–solid solubility;

(b) two-component, temperature–composition, solid–liquid diagram, one compound of formula $AB_2$ that melts incongruently, negligible solid–solid solubility;
(c) two-component, constant temperature–composition, liquid–vapour diagram, formation of an azeotrope at $x_B=0.333$, complete miscibility.

## Exercises

**5C.1(a)** The following temperature–composition data were obtained for a mixture of octane (O) and methylbenzene (M) at 1.00 atm, where $x$ is the mole fraction in the liquid and $y$ the mole fraction in the vapour at equilibrium.

| $\theta/°C$ | 110.9 | 112.0 | 114.0 | 115.8 | 117.3 | 119.0 | 121.1 | 123.0 |
|---|---|---|---|---|---|---|---|---|
| $x_M$ | 0.908 | 0.795 | 0.615 | 0.527 | 0.408 | 0.300 | 0.203 | 0.097 |
| $y_M$ | 0.923 | 0.836 | 0.698 | 0.624 | 0.527 | 0.410 | 0.297 | 0.164 |

The boiling points are 110.6 °C and 125.6 °C for M and O, respectively. Plot the temperature–composition diagram for the mixture. What is the composition of the vapour in equilibrium with the liquid of composition (i) $x_M=0.250$ and (ii) $x_O=0.250$?
**5C.1(b)** The following temperature–composition data were obtained for a mixture of two liquids A and B at 1.00 atm, where $x$ is the mole fraction in the liquid and $y$ the mole fraction in the vapour at equilibrium.

| $\theta/°C$ | 125 | 130 | 135 | 140 | 145 | 150 |
|---|---|---|---|---|---|---|
| $x_A$ | 0.91 | 0.65 | 0.45 | 0.30 | 0.18 | 0.098 |
| $y_A$ | 0.99 | 0.91 | 0.77 | 0.61 | 0.45 | 0.25 |

The boiling points are 124 °C for A and 155 °C for B. Plot the temperature/composition diagram for the mixture. What is the composition of the vapour in equilibrium with the liquid of composition (i) $x_A=0.50$ and (ii) $x_B=0.33$?

**5C.2(a)** Methylethyl ether (A) and diborane, $B_2H_6$ (B), form a compound which melts congruently at 133 K. The system exhibits two eutectics, one at 25 mol per cent B and 123 K and a second at 90 mol per cent B and 104 K. The melting points of pure A and B are 131 K and 110 K, respectively. Sketch the phase diagram for this system. Assume negligible solid–solid solubility.
**5C.2(b)** Sketch the phase diagram of the system $NH_3/N_2H_4$ given that the two substances do not form a compound with each other, that $NH_3$ freezes at –78 °C and $N_2H_4$ freezes at +2 °C, and that a eutectic is formed when the mole fraction of $N_2H_4$ is 0.07 and that the eutectic melts at –80 °C.

**5C.3(a)** Figure 5.2 shows the phase diagram for two partially miscible liquids, which can be taken to be that for water (A) and 2-methyl-1-propanol (B). Describe what will be observed when a mixture of composition $x_B=0.8$ is heated, at each stage giving the number, composition, and relative amounts of the phases present.
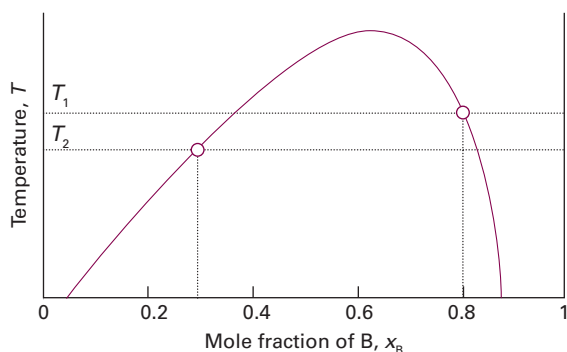


**Figure 5.2** The phase diagram for two partially miscible liquids.

**5C.2** What molecular features determine whether a mixture of two liquids will show high- and low-boiling azeotropic behaviour?

**5C.3** What factors determine the number of theoretical plates required to achieve a desired degree of separation in fractional distillation?

**5C.3(b)** Refer to Fig. 5.2 again. Describe what will be observed when a mixture of composition $x_B=0.3$ is heated, at each stage giving the number, composition, and relative amounts of the phases present.

**5C.4(a)** Indicate on the phase diagram in Fig. 5.3 the feature that denotes incongruent melting. What is the composition of the eutectic mixture and at what temperature does it melt?
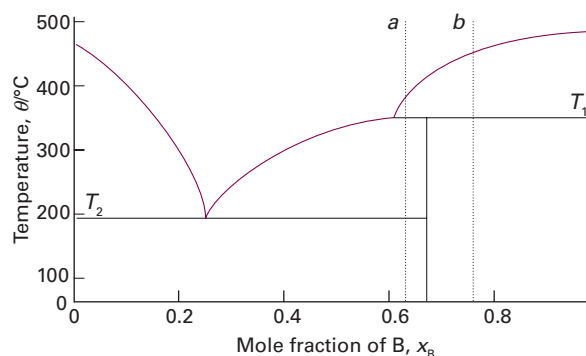


**Figure 5.3** The phase diagram referred to in Exercise 5C.4(a).

**5C.4(b)** Indicate on the phase diagram in Fig. 5.4 the feature that denotes incongruent melting. What are the compositions of any eutectic mixtures and at what temperatures do they melt?
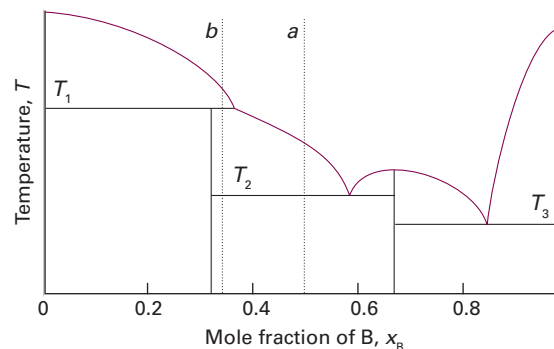


**Figure 5.4** The phase diagram referred to in Exercise 5C.4(b).

**5C.5(a)** Sketch the cooling curves for the isopleths $a$ and $b$ in Fig. 5.3.
**5C.5(b)** Sketch the cooling curves for the isopleths $a$ and $b$ in Fig. 5.4.

**5C.6(a)** Use the phase diagram in Fig. 5.3 to state (i) the solubility of Ag in Sn at 800 °C and (ii) the solubility of $Ag_3Sn$ in Ag at 460 °C, (iii) the solubility of $Ag_3Sn$ in Ag at 300 °C.
**5C.6(b)** Use the phase diagram in Fig. 5.3 to state (i) the solubility of B in A at 500 °C and (ii) the solubility of B in A at 390 °C, (iii) the solubility of $AB_2$ in B at 300 °C.

**5C.7(a)** Figure 5.5 shows the experimentally determined phase diagrams for the nearly ideal solution of hexane and heptane. (i) Label the regions of the

diagrams to which phases are present. (ii) For a solution containing 1 mol each of hexane and heptane molecules, estimate the vapour pressure at 70 °C when vaporization on reduction of the external pressure just begins. (iii) What is the vapour pressure of the solution at 70 °C when just one drop of liquid remains. (iv) Estimate from the figures the mole fraction of hexane in the liquid and vapour phases for the conditions of part b. (v) What are the mole fractions for the conditions of part c? (vi) At 85 °C and 760 Torr, what are the amounts substance in the liquid and vapour phases when $z_{heptane} = 0.40$?
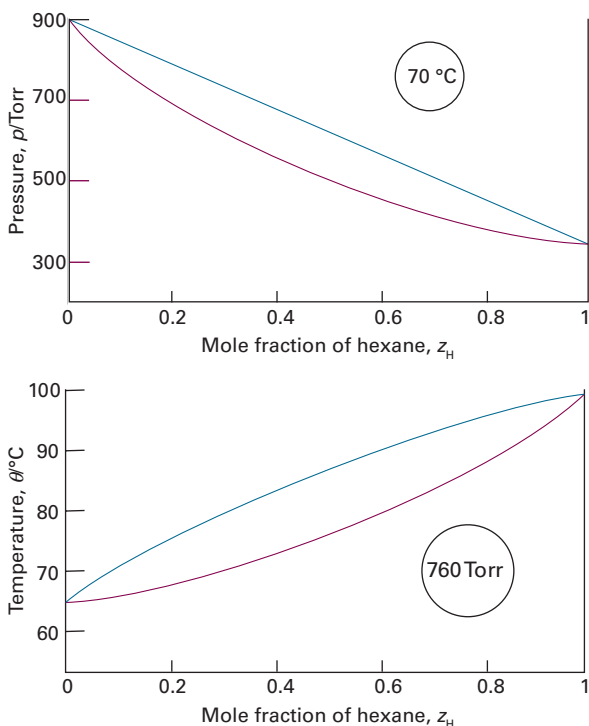


**Figure 5.5** Phase diagrams for the nearly ideal solution of hexane and heptane.

**5C.7(b)** Uranium tetrafluoride and zirconium tetrafluoride melt at 1035 °C and 912 °C respectively. They form a continuous series of solid solutions with a minimum melting temperature of 765 °C and composition $x(ZrF_4) = 0.77$. At 900 °C, the liquid solution of composition $x(ZrF_4) = 0.28$ is in equilibrium with a solid solution of composition $x(ZrF_4) = 0.14$. At 850 °C the two compositions are 0.87 and 0.90, respectively. Sketch the phase diagram for this system and state what is observed when a liquid of composition $x(ZrF_4) = 0.40$ is cooled slowly from 900 °C to 500 °C.

**5C.8(a)** Methane (melting point 91 K) and tetrafluoromethane (melting point 89 K) do not form solid solutions with each other, and as liquids they are only partially miscible. The upper critical temperature of the liquid mixture is 94 K at $x(CF_4) = 0.43$ and the eutectic temperature is 84 K at $x(CF_4) = 0.88$. At 86 K, the phase in equilibrium with the tetrafluoromethane-rich solution changes from solid methane to a methane-rich liquid. At that temperature, the two liquid solutions that are in mutual equilibrium have the compositions $x(CF_4) = 0.10$ and $x(CF_4) = 0.80$. Sketch the phase diagram.

**5C.8(b)** Describe the phase changes that take place when a liquid mixture of 4.0 mol $B_2H_6$ (melting point 131 K) and 1.0 mol $CH_3OCH_3$ (melting point 135 K) is cooled from 140 K to 90 K. These substances form a compound $(CH_3)_2OB_2H_6$ that melts congruently at 133 K. The system exhibits one eutectic at $x(B_2H_6) = 0.25$ and 123 K and another at $x(B_2H_6) = 0.90$ and 104 K.

**5C.9(a)** Refer to the information in Exercise 5C.8(a) and sketch the cooling curves for liquid mixtures in which $x(CF_4)$ is (i) 0.10, (ii) 0.30, (iii) 0.50, (iv) 0.80, and (v) 0.95.

**5C.9(b)** Refer to the information in Exercise 5C.8(b) and sketch the cooling curves for liquid mixtures in which $x(B_2H_6)$ is (i) 0.10, (ii) 0.30, (iii) 0.50, (iv) 0.80, and (v) 0.95.

**5C.10(a)** Hexane and perfluorohexane show partial miscibility below 22.70 °C. The critical concentration at the upper critical temperature is $x = 0.355$, where $x$ is the mole fraction of $C_6H_{14}$. At 22.0 °C the two solutions in equilibrium have $x = 0.24$ and $x = 0.48$, respectively, and at 21.5 °C the mole fractions are 0.22 and 0.51. Sketch the phase diagram. Describe the phase changes that occur when perfluorohexane is added to a fixed amount of hexane at (i) 23 °C, (ii) 22 °C.

**5C.10(b)** Two liquids, A and B, show partial miscibility below 52.4 °C. The critical concentration at the upper critical temperature is $x = 0.459$, where $x$ is the mole fraction of A. At 40.0 °C the two solutions in equilibrium have $x = 0.22$ and $x = 0.60$, respectively, and at 42.5 °C the mole fractions are 0.24 and 0.48. Sketch the phase diagram. Describe the phase changes that occur when B is added to a fixed amount of A at (i) 48 °C, (ii) 52.4 °C.

## Problems

**5C.1‡** 1-Butanol and chlorobenzene form a minimum-boiling azeotropic system. The mole fraction of 1-butanol in the liquid ($x$) and vapour ($y$) phases at 1.000 atm is given below for a variety of boiling temperatures (H. Artigas et al., *J. Chem. Eng. Data* **42**, 132 (1997)).

| $T/K$ | 396.57 | 393.94 | 391.60 | 390.15 | 389.03 | 388.66 | 388.57 |
|---|---|---|---|---|---|---|---|
| $x$ | 0.1065 | 0.1700 | 0.2646 | 0.3687 | 0.5017 | 0.6091 | 0.7171 |
| $y$ | 0.2859 | 0.3691 | 0.4505 | 0.5138 | 0.5840 | 0.6409 | 0.7070 |

Pure chlorobenzene boils at 404.86 K. (a) Construct the chlorobenzene-rich portion of the phase diagram from the data. (b) Estimate the temperature at which a solution for which the mole fraction of 1-butanol is 0.300 begins to boil. (c) State the compositions and relative proportions of the two phases present after a solution initially 0.300 1-butanol is heated to 393.94 K.

**5C.2‡** An, Zhao, Jiang, and Shen investigated the liquid–liquid coexistence curve of *N,N*-dimethylacetamide and heptane (X. An et al., *J. Chem. Thermodynamics* **28**, 1221 (1996)). Mole fractions of *N,N*-dimethylacetamide in the upper ($x_1$) and lower ($x_2$) phases of a two-phase region are given opposite as a function of temperature:

| $T/K$ | 309.820 | 309.422 | 309.031 | 308.006 | 306.686 |
|---|---|---|---|---|---|
| $x_1$ | 0.473 | 0.400 | 0.371 | 0.326 | 0.239 |
| $x_2$ | 0.529 | 0.601 | 0.625 | 0.657 | 0.690 |

| $T/K$ | 304.553 | 301.803 | 299.097 | 296.000 | 294.534 |
|---|---|---|---|---|---|
| $x_1$ | 0.255 | 0.218 | 0.193 | 0.168 | 0.157 |
| $x_2$ | 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,N*-dimethylacetamide with 0.250 mol of heptane at 296.0 K. To what temperature must the mixture be heated to form a single-phase mixture?

**5C.3** Phosphorus and sulfur form a series of binary compounds. The best characterized are $P_4S_3$, $P_4S_7$, and $P_4S_{10}$, all of which melt congruently. Assuming that only these three binary compounds of the two elements exist, (a) draw schematically only the P/S phase diagram. Label each region of the diagram with the substance that exists in that region and indicate its

phase. Label the horizontal axis as $x_S$ and give the numerical values of $x_S$ that correspond to the compounds. The melting point of pure phosphorus is 44 °C and that of pure sulfur is 119 °C. (b) Draw, schematically, the cooling curve for a mixture of composition $x_S = 0.28$. Assume that a eutectic occurs at $x_S = 0.2$ and negligible solid–solid solubility.

**5C.4** The following table gives the break and halt temperatures found in the cooling curves of two metals A and B. Construct a phase diagram consistent with the data of these curves. Label the regions of the diagram, stating what phases and substances are present. Give the probable formulas of any compounds that form.

| $100x_B$ | $\theta_{break}/°C$ | $\theta_{halt,1}/°C$ | $\theta_{halt,2}/°C$ |
|---|---|---|---|
| 0 | | 1100 | |
| 10.0 | 1060 | 700 | |
| 20.0 | 1000 | 700 | |
| 30.0 | 940 | 700 | 400 |
| 40.0 | 850 | 700 | 400 |
| 50.0 | 750 | 700 | 400 |
| 60.0 | 670 | 400 | |
| 70.0 | 550 | 400 | |
| 80.0 | | 400 | |
| 90.0 | 450 | 400 | |
| 100.0 | | 500 | |

**5C.5** Consider the phase diagram in Fig. 5.6, which represents a solid–liquid equilibrium. Label all regions of the diagram according to the chemical species that exist in that region and their phases. Indicate the number of species and phases present at the points labelled $b$, $d$, $e$, $f$, $g$, and $k$. Sketch cooling curves for compositions $x_B = 0.16$, 0.23, 0.57, 0.67, and 0.84.
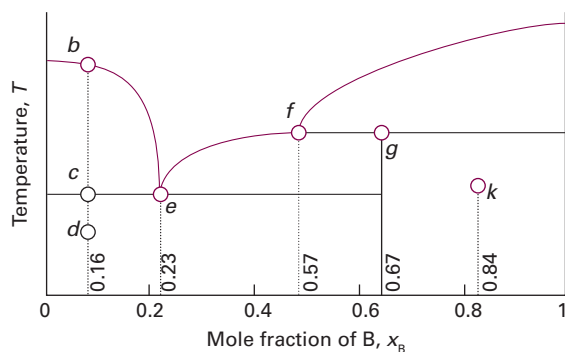


**Figure 5.6** The phase diagram referred to in Problem 5C.5.

**5C.6** Sketch the phase diagram for the Mg/Cu system using the following information: $\theta_f(Mg) = 648$ °C, $\theta_f(Cu) = 1085$ °C; two intermetallic compounds are formed with $\theta_f(MgCu_2) = 800$ °C and $\theta_f(Mg_2Cu) = 580$ °C; eutectics of mass percentage Mg composition and melting points 10 per cent (690 °C), 33 per cent (560 °C), and 65 per cent (380 °C). A sample of Mg/Cu alloy containing 25 per cent Mg by mass was prepared in a crucible heated to 800 °C in an

inert atmosphere. Describe what will be observed if the melt is cooled slowly to room temperature. Specify the composition and relative abundances of the phases and sketch the cooling curve.

**5C.7‡** The temperature–composition diagram for the Ca/Si binary system is shown in Fig. 5.7. (a) Identify eutectics, congruent melting compounds, and incongruent melting compounds. (b) If a 20 per cent by atom composition melt of silicon at 1500 °C is cooled to 1000 °C, what phases (and phase composition) would be at equilibrium? Estimate the relative amounts of each phase. (c) Describe the equilibrium phases observed when an 80 per cent by atom composition Si melt is cooled to 1030 °C. What phases, and relative amounts, would be at equilibrium at a temperature (i) slightly higher than 1030 °C, (ii) slightly lower than 1030 °C? Draw a graph of the mole percentages of both Si(s) and CaSi$_2$(s) as a function of mole percentage of melt that is freezing at 1030 °C.
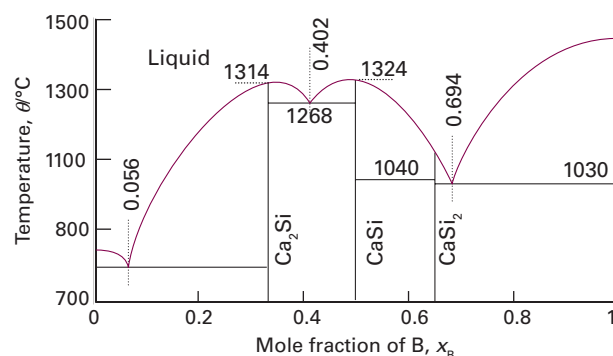


**Figure 5.7** The temperature–composition diagram for the Ca/Si binary system.

**5C.8** Iron(II) chloride (melting point 677 °C) and potassium chloride (melting point 776 °C) form the compounds KFeCl$_3$ and K$_2$FeCl$_4$ at elevated temperatures. KFeCl$_3$ melts congruently at 380 °C and K$_2$FeCl$_4$ melts incongruently at 399 °C. Eutectics are formed with compositions $x = 0.38$ (melting point 351 °C) and $x = 0.54$ (melting point 393 °C), where $x$ is the mole fraction of FeCl$_2$. The KCl solubility curve intersects the K$_2$FeCl$_4$ curve at $x = 0.34$. Sketch the phase diagram. State the phases that are in equilibrium when a mixture of composition $x = 0.36$ is cooled from 400 °C to 300 °C.

**5C.9** To reproduce the results of Fig. 5C.2, first rearrange eqn 5C.4 so that $y_A$ is expressed as a function of $x_A$ and the ratio $p_A^*/p_B^*$. Then plot $y_A$ against $x_A$ for several values of ratio $p_A^*/p_B^* > 1$.

**5C.10** To reproduce the results of Fig. 5C.3, first rearrange eqn 5C.5 so that the ratio $p_A^*/p_B^*$ is expressed as a function of $y_A$ and the ratio $p_A^*/p_B^*$. Then plot $p_A/p_A^*$ against $y_A$ for several values of $p_A^*/p_B^* > 1$.

**5C.11** Working from eqn 5B.7, write an expression for $T_{min}$, the temperature at which $\Delta_{mix}G$ has a minimum, as a function of $\xi$ and $x_A$. Then, plot $T_{min}$ against $x_A$ for several values of $\xi$. Provide a physical interpretation for any maxima or minima that you observe in these plots.

**5C.12** Use eqn 5C.7 to generate plots of $\xi$ against $x_A$ by one of two methods: (a) solve the transcendental equation $\ln\{(x/(1-x)\} + \xi(1-2x) = 0$ numerically, or (b) plot the first term of the transcendental equation against the second and identify the points of intersection as $\xi$ is changed.

# TOPIC 5D  Phase diagrams of ternary systems

## Discussion questions

**5D.1** What is the maximum number of phases that can be in equilibrium in a ternary system?

**5D.2** Does the lever rule apply to a ternary system?

**5D.3** Could a regular tetrahedron be used to depict the properties of a four-component system?

## Exercises

**5D.1(a)** Mark the following features on triangular coordinates: (i) the point (0.2, 0.2, 0.6), (ii) the point (0, 0.2, 0.8), (iii) the point at which all three mole fractions are the same.

**5D.1(b)** Mark the following features on triangular coordinates: (i) the point (0.6, 0.2, 0.2), (ii) the point (0.8, 0.2, 0), (iii) the point (0.25, 0.25, 0.50).

**5D.2(a)** Mark the following points on a ternary phase diagram for the system $NaCl/Na_2SO_4 \cdot 10H_2O/H_2O$: (i) 25 per cent by mass NaCl, 25 per cent $Na_2SO_4 \cdot 10H_2O$, and the rest $H_2O$; (ii) the line denoting the same relative composition of the two salts but with changing amounts of water.

**5D.2(b)** Mark the following points on a ternary phase diagram for the system $NaCl/Na_2SO_4 \cdot 10H_2O/H_2O$: (i) 33 per cent by mass NaCl, 33 per cent $Na_2SO_4 \cdot 10H_2O$, and the rest $H_2O$; (ii) the line denoting the same relative composition of the two salts but with changing amounts of water.

**5D.3(a)** Refer to the ternary phase diagram in Fig. 5D.4. How many phases are present, and what are their compositions and relative abundances, in a mixture that contains 2.3 g of water, 9.2 g of chloroform, and 3.1 g of acetic acid? Describe what happens when (i) water, (iii) acetic acid is added to the mixture.

**5D.3(b)** Refer to the ternary phase diagram in Fig. 5D.4. How many phases are present, and what are their compositions and relative abundances, in a mixture that contains 55.0 g of water, 8.8 g of chloroform, and 3.7 g of acetic acid? Describe what happens when (i) water, (ii) acetic acid is added to the mixture.

**5D.4(a)** Figure 5.8 shows the phase diagram for the ternary system $NH_4Cl/(NH_4)_2SO_4/H_2O$ at 25 °C. Identify the number of phases present for mixtures of compositions (i) (0.2, 0.4, 0.4), (ii) (0.4, 0.4, 0.2), (iii) (0.2, 0.1, 0.7), (iv) (0.4, 0.16, 0.44). The numbers are mole fractions of the three components in the order $(NH_4Cl,(NH_4)_2SO_4,H_2O)$.
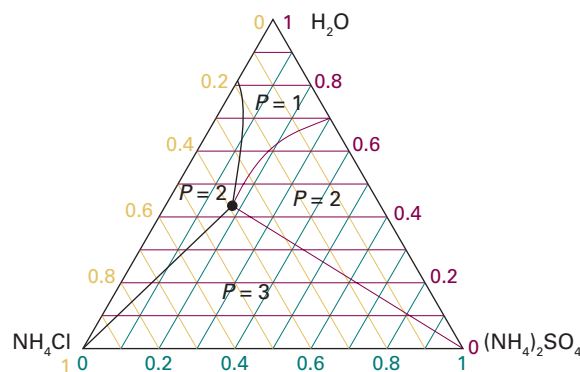


**Figure 5.8** The phase diagram for the ternary system $NH_4Cl/(NH_4)_2SO_4/H_2O$ at 25 °C.

**5D.4(b)** Refer to Fig. 5.8 and identify the number of phases present for mixtures of compositions (i) (0.4, 0.1, 0.5), (ii) (0.8, 0.1, 0.1), (iii) (0, 0.3,0.7), (iv) (0.33, 0.33, 0.34). The numbers are mole fractions of the three components in the order $(NH_4Cl,(NH_4)_2SO_4,H_2O)$.

**5D.5(a)** Referring to Fig. 5.8, deduce the molar solubility of (i) $NH_4Cl$, (ii) $(NH_4)_2SO_4$ in water at 25 °C.

**5D.5(b)** Describe what happens when (i) $(NH_4)_2SO_4$ is added to a saturated solution of $NH_4Cl$ in water in the presence of excess $NH_4Cl$, (ii) water is added to a mixture of 25 g of $NH_4Cl$ and 75 g of $(NH_4)_2SO_4$.

## Problems

**5D.1** At a certain temperature, the solubility of $I_2$ in liquid $CO_2$ is $x(I_2) = 0.03$. At the same temperature its solubility in nitrobenzene is 0.04. Liquid carbon dioxide and nitrobenzene are miscible in all proportions, and the solubility of $I_2$ in the mixture varies linearly with the proportion of nitrobenzene. Sketch a phase diagram for the ternary system.

**5D.2** The binary system nitroethane/decahydronaphthalene (DEC) shows partial miscibility, with the two-phase region lying between $x = 0.08$ and $x = 0.84$, where $x$ is the mole fraction of nitroethane. The binary system liquid carbon dioxide/DEC is also partially miscible, with its two-phase region lying between $y = 0.36$ and $y = 0.80$, where $y$ is the mole fraction of DEC. Nitroethane and liquid carbon dioxide are miscible in all proportions.

The addition of liquid carbon dioxide to mixtures of nitroethane and DEC increases the range of miscibility, and the plait point is reached when $z$, the mole fraction of $CO_2$, is 0.18 and $x = 0.53$. The addition of nitroethane to mixtures of carbon dioxide and DEC also results in another plait point at $x = 0.08$ and $y = 0.52$. (a) Sketch the phase diagram for the ternary system, (b) For some binary mixtures of nitroethane and liquid carbon dioxide the addition of arbitrary amounts of DEC will not cause phase separation. Find the range of concentration for such binary mixtures.

**5D.3** Prove that a straight line from the apex A of a ternary phase diagram to the opposite edge BC represents mixtures of constant ratio of B and C, however much A is present.

# TOPIC 5E  Activities

## Discussion questions

**5E.1** What are the contributions that account for the difference between activity and concentration?

**5E.2** How is Raoult's law modified so as to describe the vapour pressure of real solutions?

**5E.3** Summarize the ways in which activities may be measured.

## Exercises

**5E.1(a)** Substances A and B are both volatile liquids with $p_A^* = 300$ Torr, $p_B^* = 250$ Torr, and $K_B = 200$ Torr (concentration expressed in mole fraction). When $x_A = 0.9$, $b_B = 2.22$ mol kg$^{-1}$, $p_A = 250$ Torr, and $p_B = 25$ Torr. Calculate the activities and activity coefficients of A and B. Use the mole fraction, Raoult's law basis system for A and the Henry's law basis system (both mole fractions and molalities) for B.

**5E.1(b)** Given that $p^*(H_2O)=0.02308$ atm and $p(H_2O)=0.02239$ atm in a solution in which 0.122 kg of a involatile solute ($M=241$ g mol⁻¹) is dissolved in 0.920 kg water at 293 K, calculate the activity and activity coefficient of water in the solution.

**5E.2(a)** By measuring the equilibrium between liquid and vapour phases of an acetone(A)/methanol(M) solution at 57.2 °C at 1.00 atm, it was found that $x_A=0.400$ when $y_A=0.516$. Calculate the activities and activity coefficients of both components in this solution on the Raoult's law basis. The vapour pressures of the pure components at this temperature are: $p_A^*=105$ kPa and $p_M^*=73.5$ kPa . ($x_A$ is the mole fraction in the liquid and $y_A$ the mole fraction in the vapour.)
**5E.2(b)** By measuring the equilibrium between liquid and vapour phases of a solution at 30 °C at 1.00 atm, it was found that $x_A=0.220$ when $y_A=0.314$.

Calculate the activities and activity coefficients of both components in this solution on the Raoult's law basis. The vapour pressures of the pure components at this temperature are: $p_A^*=73.0$ kPa and $p_B^*=92.1$ kPa. ($x_A$ is the mole fraction in the liquid and $y_A$ the mole fraction in the vapour.)

**5E.3(a)** Find the relation between the standard and biological standard Gibbs energies of a reaction of the form $A \rightarrow 2B+2\,H^+(aq)$.
**5E.3(b)** Find the relation between the standard and biological standard Gibbs energies of a reaction of the form $2\,A \rightarrow B+4\,H^+(aq)$.

**5E.4(a)** Suppose it is found that for a hypothetical regular solution that $\xi=1.40$, $p_A^*=15.0$ kPa and $p_B^*=11.6$ kPa. Draw the vapour-pressure diagram.
**5E.4(b)** Suppose it is found that for a hypothetical regular solution that $\xi=-1.40$, $p_A^*=15.0$ kPa and $p_B^*=11.6$ kPa . Draw the vapour-pressure diagram.

## Problems

**5E.1‡** Francesconi, Lunelli, and Comelli studied the liquid–vapour equilibria of trichloromethane and 1,2-epoxybutane at several temperatures (Francesconi et al., *J. Chem. Eng. Data* **41**, 310 (1996)). Among their data are the following measurements of the mole fractions of trichloromethane in the liquid phase ($x_T$) and the vapour phase ($y_T$) at 298.15 K as a function of pressure.

| p/kPa | 23.40 | 21.75 | 20.25 | 18.75 | 18.15 | 20.25 | 22.50 | 26.30 |
|---|---|---|---|---|---|---|---|---|
| x | 0 | 0.129 | 0.228 | 0.353 | 0.511 | 0.700 | 0.810 | 1 |
| y | 0 | 0.065 | 0.145 | 0.285 | 0.535 | 0.805 | 0.915 | 1 |

Compute the activity coefficients of both components on the basis of Raoult's law.

**5E.2** The *osmotic coefficient* $\phi$ is defined as $\phi=-(x_A/x_B)\ln a_A$. By writing $r=x_B/x_A$, and using the Gibbs–Duhem equation, show that we can calculate the activity of B from the activities of A over a composition range by using the formula

$$\ln \frac{a_B}{r}=\phi-\phi(0)+\int_0^r \frac{\phi-1}{r}dr$$

**5E.3** Show that the osmotic pressure of a real solution is given by $\Pi V=-RT\ln a_A$. Go on to show that, provided the concentration of the solution is low, this expression takes the form $\Pi V=\phi RT[B]$ and hence that the osmotic coefficient $\phi$ (which is defined in Problem 5E.2) may be determined from osmometry.

**5E.4** Use mathematical software, a spreadsheet, or the *Living graphs* on the web site for this book to plot $p_A/p_A^*$ against $x_A$ with $\xi=2.5$ by using eqn 5E.19 and then eqn 5E.20. Above what value of $x_A$ do the values of $p_A/p_A^*$ given by these equations differ by more than 10 per cent?

# TOPIC 5F  The activities of ions

## Discussion questions

**5F.1** Why do the activity coefficients of ions in solution differ from 1? Why are they less than 1 in dilute solutions?

**5F.2** Describe the general features of the Debye–Hückel theory of electrolyte solutions.

**5F.3** Suggest an interpretation of the additional terms in extended versions of the Debye–Hückel limiting law.

## Exercises

**5F.1(a)** Calculate the ionic strength of a solution that is 0.10 mol kg⁻¹ in KCl(aq) and 0.20 mol kg⁻¹ in CuSO₄(aq).
**5F.1(b)** Calculate the ionic strength of a solution that is 0.040 mol kg⁻¹ in K₃[Fe(CN)₆](aq), 0.030 mol kg⁻¹ in KCl(aq), and 0.050 mol kg⁻¹ in NaBr(aq).

**5F.2(a)** Calculate the masses of (i) Ca(NO₃)₂ and, separately, (ii) NaCl to add to a 0.150 mol kg⁻¹ solution of KNO₃(aq) containing 500 g of solvent to raise its ionic strength to 0.250.
**5F.2(b)** Calculate the masses of (i) KNO₃ and, separately, (ii) Ba(NO₃)₂ to add to a 0.110 mol kg⁻¹ solution of KNO₃(aq) containing 500 g of solvent to raise its ionic strength to 1.00.

**5F.3(a)** Estimate the mean ionic activity coefficient and activity of a solution at 25 °C that is 0.010 mol kg⁻¹ CaCl₂(aq) and 0.030 mol kg⁻¹ NaF(aq).
**5F.3(b)** Estimate the mean ionic activity coefficient and activity of a solution at 25 °C that is 0.020 mol kg⁻¹ NaCl(aq) and 0.035 mol kg⁻¹ Ca(NO₃)₂(aq).

**5F.4(a)** The mean activity coefficients of HBr in three dilute aqueous solutions at 25 °C are 0.930 (at 5.0 mmol kg⁻¹), 0.907 (at 10.0 mmol kg⁻¹), and 0.879 (at 20.0 mmol kg⁻¹). Estimate the value of *B* in eqn 5F.11a.
**5F.4(b)** The mean activity coefficients of KCl in three dilute aqueous solutions at 25 °C are 0.927 (at 5.0 mmol kg⁻¹), 0.902 (at 10.0 mmol kg⁻¹), and 0.816 (at 50.0 mmol kg⁻¹). Estimate the value of *B* in eqn 5F.11a.

## Problems

**5F.1** The mean activity coefficients for aqueous solutions of NaCl at 25 °C are given opposite. Confirm that they support the Debye–Hückel limiting law and that an improved fit is obtained with the Davies equation.

| $b/(\text{mmol kg}^{-1})$ | 1.0 | 2.0 | 5.0 | 10.0 | 20.0 |
|---|---|---|---|---|---|
| $\gamma_\pm$ | 0.9649 | 0.9519 | 0.9275 | 0.9024 | 0.8712 |

**5F.2** Consider the plot of log $\gamma_\pm$ against $I^{1/2}$ with $B=1.50$ and $C=0$ in the Davies equation as a representation of experimental data for a certain MX electrolyte. Over what range of ionic strengths does the application of the limiting law lead to an error in the value of the activity coefficient of less than 10 per cent of the value predicted by the extended law?

# Integrated activities

**5.1** The table below lists the vapour pressures of mixtures of iodoethane (I) and ethyl acetate (A) at 50 °C. Find the activity coefficients of both components on (a) the Raoult's law basis, (b) the Henry's law basis with iodoethane as solute.

| $x_I$ | 0 | 0.0579 | 0.1095 | 0.1918 | 0.2353 | 0.3718 |
|---|---|---|---|---|---|---|
| $p_I$/kPa | 0 | 3.73 | 7.03 | 11.7 | 14.05 | 20.72 |
| $p_A$/kPa | 37.38 | 35.48 | 33.64 | 30.85 | 29.44 | 25.05 |

| $x_I$ | 0.5478 | 0.6349 | 0.8253 | 0.9093 | 1.0000 |
|---|---|---|---|---|---|
| $p_I$/kPa | 28.44 | 31.88 | 39.58 | 43.00 | 47.12 |
| $p_A$/kPa | 19.23 | 16.39 | 8.88 | 5.09 | 0 |

**5.2** Plot the vapour pressure data for a mixture of benzene (B) and acetic acid (A) given below and plot the vapour pressure/composition curve for the mixture at 50 °C. Then confirm that Raoult's and Henry's laws are obeyed in the appropriate regions. Deduce the activities and activity coefficients of the components on the Raoult's law basis and then, taking B as the solute, its activity and activity coefficient on a Henry's law basis. Finally, evaluate the excess Gibbs energy of the mixture over the composition range spanned by the data.

| $x_A$ | 0.0160 | 0.0439 | 0.0835 | 0.1138 | 0.1714 |
|---|---|---|---|---|---|
| $p_A$/kPa | 0.484 | 0.967 | 1.535 | 1.89 | 2.45 |
| $p_B$/kPa | 35.05 | 34.29 | 33.28 | 32.64 | 30.90 |

| $x_A$ | 0.2973 | 0.3696 | 0.5834 | 0.6604 | 0.8437 | 0.9931 |
|---|---|---|---|---|---|---|
| $p_A$/kPa | 3.31 | 3.83 | 4.84 | 5.36 | 6.76 | 7.29 |
| $p_B$/kPa | 28.16 | 26.08 | 20.42 | 18.01 | 10.0 | 0.47 |

**5.3‡** Chen and Lee studied the liquid–vapour equilibria of cyclohexanol with several gases at elevated pressures (J.-T. Chen and M.-J. Lee, *J. Chem. Eng. Data* **41**, 339 (1996)). Among their data are the following measurements of the mole fractions of cyclohexanol in the vapour phase ($y$) and the liquid phase ($x$) at 393.15 K as a function of pressure.

| $p$/bar | 10.0 | 20.0 | 30.0 | 40.0 | 60.0 | 80.0 |
|---|---|---|---|---|---|---|
| $y_{cyc}$ | 0.0267 | 0.0149 | 0.0112 | 0.009 47 | 0.008 35 | 0.009 21 |
| $x_{cyc}$ | 0.9741 | 0.9464 | 0.9204 | 0.892 | 0.836 | 0.773 |

Determine the Henry's law constant of $CO_2$ in cyclohexanol, and compute the activity coefficient of $CO_2$.

**5.4‡** The following data have been obtained for the liquid–vapour equilibrium compositions of mixtures of nitrogen and oxygen at 100 kPa.

| $T$/K | 77.3 | 78 | 80 | 82 | 84 | 86 | 88 | 90.2 |
|---|---|---|---|---|---|---|---|---|
| $x(O_2)$ | 0 | 10 | 34 | 54 | 70 | 82 | 92 | 100 |
| $y(O_2)$ | 0 | 2 | 11 | 22 | 35 | 52 | 73 | 100 |
| $p^*(O_2)$/Torr | 154 | 171 | 225 | 294 | 377 | 479 | 601 | 760 |

Plot the data on a temperature–composition diagram and determine the extent to which it fits the predictions for an ideal solution by calculating the activity coefficients of $O_2$ at each composition.

**5.5** Use the Gibbs–Duhem equation to derive the *Gibbs–Duhem–Margules equation*

$$\left(\frac{\partial \ln f_A}{\partial \ln x_A}\right)_{p,T} = \left(\frac{\partial \ln f_B}{\partial \ln x_B}\right)_{p,T}$$

where $f$ is the fugacity. Use the relation to show that when the fugacities are replaced by pressures, that if Raoult's law applies to one component in a mixture it must also apply to the other.

**5.6** Use the Gibbs–Duhem equation to show that the partial molar volume (or any partial molar property) of a component B can be obtained if the partial molar volume (or other property) of A is known for all compositions up to the one of interest. Do this by proving that

$$V_B = V_B^* - \int_{V_A^*}^{V_A} \frac{x_A}{1-x_A} dV_A$$

where the $x_A$ are functions of the $V_A$. Use the following data (which are for 298 K) to evaluate the integral graphically to find the partial molar volume of acetone at $x=0.500$.

| $x(CHCl_3)$ | 0 | 0.194 | 0.385 | 0.559 | 0.788 | 0.889 | 1.000 |
|---|---|---|---|---|---|---|---|
| $V_m/(cm^3\,mol^{-1})$ | 73.99 | 75.29 | 76.50 | 77.55 | 79.08 | 79.82 | 80.67 |

**5.7** Show that the freezing-point depression of a real solution in which the solvent of molar mass $M$ has activity $a_A$ obeys

$$\frac{d \ln a_A}{d(\Delta T)} = -\frac{M}{K_f}$$

and use the Gibbs–Duhem equation to show that

$$\frac{d \ln a_B}{d(\Delta T)} = -\frac{1}{b_B K_f}$$

where $a_B$ is the solute activity and $b_B$ is its molality. Use the Debye–Hückel limiting law to show that the osmotic coefficient ($\phi$, Problem 5E.2) is given by $\phi = 1 - \frac{1}{3} A'I$ with $A' = 2.303A$ and $I = b/b^\ominus$.

**5.8** For the calculation of the solubility $c$ of a gas in a solvent, it is often convenient to use the expression $c = Kp$, where $K$ is the Henry's law constant. Breathing air at high pressures, such as in scuba diving, results in an increased concentration of dissolved nitrogen. The Henry's law constant for the solubility of nitrogen is 0.18 µg/(g $H_2O$ atm). What mass of nitrogen is dissolved in 100 g of water saturated with air at 4.0 atm and 20 °C? Compare your answer to that for 100 g of water saturated with air at 1.0 atm. (Air is 78.08 mole per cent $N_2$.) If nitrogen is four times as soluble in fatty tissues as in water, what is the increase in nitrogen concentration in fatty tissue in going from 1 atm to 4 atm?

**5.9** Dialysis may be used to study the binding of small molecules to macromolecules, such as an inhibitor to an enzyme, an antibiotic to DNA, and any other instance of cooperation or inhibition by small molecules attaching to large ones. To see how this is possible, suppose inside the dialysis bag the molar concentration of the macromolecule M is [M] and the total concentration of small molecule A is $[A]_{in}$. This total concentration is the sum of the concentrations of free A and bound A, which we write $[A]_{free}$ and $[A]_{bound}$, respectively. At equilibrium, $\mu_{A,free} = \mu_{A,out}$, which implies that $[A]_{free} = [A]_{out}$, provided the activity coefficient of A is the same in both solutions. Therefore, by measuring the concentration of A in the solution outside the bag, we can find the concentration of unbound A in the macromolecule solution and, from the difference $[A]_{in} - [A]_{free} = [A]_{in} - [A]_{out}$, the concentration of bound A. Now we explore the quantitative consequences of the experimental arrangement just described.

(a) The average number of A molecules bound to M molecules, $\nu$, is

$$\nu = \frac{[A]_{bound}}{[M]} = \frac{[A]_{in} - [A]_{out}}{[M]}$$

The bound and unbound A molecules are in equilibrium, $M + A \rightleftharpoons MA$. Recall from introductory chemistry that we may write the equilibrium constant for binding, $K$, as

$$K = \frac{[MA]}{[M]_{free}[A]_{free}}$$

Now show that

$$K = \frac{\nu}{(1-\nu)[A]_{out}}$$

(b) If there are $N$ *identical* and *independent* binding sites on each macromolecule, each macromolecule behaves like $N$ separate smaller macromolecules, with the same value of $K$ for each site. It follows that the average number of A molecules per site is $\nu/N$. Show that, in this case, we may write the *Scatchard equation*:

$$\frac{\nu}{[A]_{out}} = KN - K\nu$$

(c) To apply the Scatchard equation, consider the binding of ethidium bromide ($E^-$) to a short piece of DNA by a process called *intercalation*, in which the aromatic ethidium cation fits between two adjacent DNA base pairs. An equilibrium dialysis experiment was used to study the binding of ethidium bromide (EB) to a short piece of DNA. A $1.00\ \mu mol\ dm^{-3}$ aqueous solution of the DNA sample was dialysed against an excess of EB. The following data were obtained for the total concentration of EB:

$[EB]/(\mu mol\ dm^{-3})$

| | | | | | |
|---|---|---|---|---|---|
| Side without DNA | 0.042 | 0.092 | 0.204 | 0.526 | 1.150 |
| Side with DNA | 0.292 | 0.590 | 1.204 | 2.531 | 4.150 |

From these data, make a Scatchard plot and evaluate the intrinsic equilibrium constant, $K$, and total number of sites per DNA molecule. Is the identical and independent sites model for binding applicable?

**5.10** The form of the Scatchard equation given Problem 5.9 applies only when the macromolecule has identical and independent binding sites. For non-identical independent binding sites, the Scatchard equation is

$$\frac{\nu}{[A]_{out}} = \sum_i \frac{N_i K_i}{1 + K_i[A]_{out}}$$

Plot $\nu/[A]$ for the following cases. (a) There are four independent sites on an enzyme molecule and the intrinsic binding constant is $K = 1.0 \times 10^7$. (b) There are a total of six sites per polymer. Four of the sites are identical and have an intrinsic binding constant of $1 \times 10^5$. The binding constants for the other two sites are $2 \times 10^6$.

**5.11** The addition of a small amount of a salt, such as $(NH_4)_2SO_4$, to a solution containing a charged protein increases the solubility of the protein in water. This observation is called the *salting-in effect*. However, the addition of large amounts of salt can decrease the solubility of the protein to such an extent that the protein precipitates from solution. This observation is called the *salting-out effect* and is used widely by biochemists to isolate and purify proteins. Consider the equilibrium $PX_\nu(s) \rightleftharpoons P^{\nu+}(aq) + \nu\ X^-(aq)$, where $P^{\nu+}$ is a polycationic protein of charge $\nu+$ and $X^-$ is its counter ion. Use Le Chatelier's principle and the physical principles behind the Debye–Hückel theory to provide a molecular interpretation for the salting-in and salting-out effects.

**5.12** Some polymers can form liquid crystal mesophases with unusual physical properties. For example, liquid crystalline Kevlar (**1**) is strong enough to be the material of choice for bulletproof vests and is stable at temperatures up to 600 K. What molecular interactions contribute to the formation, thermal stability, and mechanical strength of liquid crystal mesophases in Kevlar?



**1** Kevlar