CHAPTER 5

SOLUTIONS, ESPECIALLY DILUTE SOLUTIONS

§5.01 *Introduction*

There is no fundamental difference between a liquid mixture and a solution. The difference is in the manner of description. In the description of mixtures in the previous chapter all the constituent species were treated in a like manner. In the description of solutions in the present chapter we shall on the contrary single out one species which we call the solvent. All the remaining species are called solutes. There is no rigid rule to determine which species shall be regarded as solvent, but it is usually the species present in the highest proportion, at least among those species which are liquid in the pure state at the given temperature and pressure. For example we should at room temperature speak of water as solvent and urea as solute, even if the urea were in excess, because pure urea at room temperature is a solid.

We shall always denote the solvent by the subscript $_1$ and the solutes by the subscripts $_2$, $_3$, . . . in particular or by the general subscript $_s$.

§5.02 *Mole ratios and molalities*

We consider a phase containing an amount n_1 of the species 1, an amount n_2 of the species 2, and so on. When considering such a phase as a mixture we described the composition by the fractions $n_1/\Sigma_i n_i$, $n_2/\Sigma_i n_i$ and so on. When considering this phase as a solution we shall on the contrary describe its composition by the ratios n_2/n_1, n_3/n_1 and so on.

While the fractions $n_1/\Sigma_i n_i$, $n_2/\Sigma_i n_i$ were denoted by x_1, $x_2, \ldots$ and were called *mole fractions*, the fractions n_2/n_1, $n_3/n_1, \ldots$ will be denoted by r_2, $r_3, \ldots$ and will be called *solute–solvent mole ratios.* In a phase of c component species there are c different mole fractions, which we recall are related by $\Sigma_i x_i = 1$ so that only c − 1 are independent. There are only c − 1 mole ratios $r_2, r_3, \ldots r_c$ and these are all independent. We shall use these as the independent variables together with T and P.

For all purposes of general theory we shall use the variables $r_2, r_3, \ldots r_c$ together with T, P. For practical purposes, it is customary to use instead of r_s a quantity m_s directly proportional to r_s defined by

$$m_s = r_s/r^\ominus \qquad 5.02.1$$

where $r^\ominus$ is a standard value of r_s customarily and here defined by

$$r^\ominus = M_1/\text{kg mole}^{-1} \qquad 5.02.2$$

where M_1 is the proper mass of the solvent. It follows that $r_s = r^\ominus$ when there is one mole of the solute s for each kilogramme of solvent. Thus defined, r_s, $r^\ominus$, and m_s are all dimensionless. This quantity m_s is called *molality*. We shall derive most of our formulae in terms of the mole ratios r and shall transcribe only a few important ones into terms of molalities m by use of (1). The mole fractions x and mole ratios r are interrelated by

$$r_2 = x_2/x_1 = x_2/(1 - \sum_s x_s) \qquad 5.02.3$$

$$x_2 = r_2/(1 + \sum_s r_s) \qquad 5.02.4$$

and similar relations for the other solute species. We also note the relation

$$(1 + \sum_s r_s)(1 - \sum_s x_s) = 1. \qquad 5.02.5$$

§5.03 *Partial and apparent quantities*

If X denotes any extensive property such as $V, U, S, \text{Æ}, G$ then the corresponding partial quantities are defined in §4.03 by

$$X_1 = (\partial X/\partial n_1)_{T, P, n_2, n_3}, \ldots \qquad 5.03.1$$

$$X_s = (\partial X/\partial n_s)_{T, P, n_1, n_2}, \ldots. \qquad 5.03.2$$

According to (4.03.6) these are interrelated by

$$n_1 \mathrm{d}X_1 + \sum_s n_s \mathrm{d}X_s = 0 \qquad (T, P \text{ const.}). \qquad 5.03.3$$

Dividing (3) by n_1 we have

$$\mathrm{d}X_1 + \sum_s r_s \mathrm{d}X_s = 0 \qquad (T, P \text{ const.}). \qquad 5.03.4$$

In particular, if there is only one solute species 2 formula (4) reduces to

$$\partial X_1/\partial r + r\partial X_2/\partial r = 0 \qquad (T, P \text{ const.}). \qquad 5.03.5$$

When there is only one solute species 2 the quantity X_ϕ defined by

$$n_2 X_\phi = X - n_1 X_1^0 \qquad 5.03.6$$

where X_1^0 denotes the proper X of the pure solvent, is called the *apparent proper X of the solute**. We can obtain the relation between X_ϕ and X_2 by differentiating (6) with respect to n_2 keeping n_1 constant. We find

$$X_2 = \partial X/\partial n_2 = X_\phi + n_2(\partial X_\phi/\partial n_2)_{n_1} = X_\phi + r\,\mathrm{d}X_\phi/\mathrm{d}r. \qquad 5.03.7$$

There is no such quantity as X_ϕ when there is more than one solute species.

We recall the important relations between the several partial quantities in §4.04. These apply both to the partial quantities of the solvent and to those of the solute species.

We also recall the important equality (1.28.11) which holds both for the solvent and for the solute species

$$\mu_1 = G_1 \qquad \mu_s = G_s \qquad 5.03.8$$

with the consequent relations

$$\partial\mu_1/\partial T = -S_1 \qquad \partial\mu_s/\partial T = -S_s \qquad 5.03.9$$

$$\partial \ln \lambda_1/\partial T = -H_1/RT^2 \qquad \partial \ln \lambda_s/\partial T = -H_s/RT^2 \qquad 5.03.10$$

$$\partial\mu_1/\partial P = V_1 \qquad \partial\mu_s/\partial P = V_s. \qquad 5.03.11$$

§5.04 *Gibbs–Duhem relation*

We recall the Gibbs–Duhem relation

$$n_1\mathrm{d}\mu_1 + \sum_s n_s\mathrm{d}\mu_s = 0 \qquad (T, P \text{ const.}) \qquad 5.04.1$$

or

$$n_1\mathrm{d}\ln\lambda_1 + \sum_s n_s\mathrm{d}\ln\lambda_s = 0 \qquad (T, P \text{ const.}). \qquad 5.04.2$$

Dividing through by n_1 we obtain the alternative form

$$\mathrm{d}\mu_1 + \sum_s r_s\mathrm{d}\mu_s = 0 \qquad (T, P \text{ const.}) \qquad 5.04.3$$

or

$$\mathrm{d}\ln\lambda_1 + \sum_s r_s\mathrm{d}\ln\lambda_s = 0 \qquad (T, P \text{ const.}). \qquad 5.04.4$$

In the case of a single solute (3) reduces to

$$\mathrm{d}\mu_1/\mathrm{d}r + r\,\mathrm{d}\mu_2/\mathrm{d}r = 0 \qquad (T, P \text{ const.}) \qquad 5.04.5$$

or

$$\mathrm{d}\ln\lambda_1/\mathrm{d}r + r\,\mathrm{d}\ln\lambda_2/\mathrm{d}r = 0 \qquad (T, P \text{ const.}). \qquad 5.04.6$$

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* The notation ϕ_v used by some authors instead of V_ϕ is deplorable.

§5.05 *Partial quantities at high dilution*

If X denotes any extensive property, so that X_1, X_2 are the corresponding partial quantities in a solution of a single solute, we have according to (5.03.5)

$$\partial X_1/\partial r + r\partial X_2/\partial r = 0 \qquad (T, P \text{ const.}). \qquad 5.05.1$$

It follows that when $r \to 0$ either $\partial X_1/\partial r \to 0$ or $\partial X_2/\partial r \to \infty$. The former case occurs when X denotes V or U or H; the latter occurs when X denotes S or $Æ$ or G.

§5.06 *Ideal dilute solutions*

Let us consider a solution of a volatile solute 2 in the solvent 1 so dilute that $n_2 \ll n_1$. It is then physically obvious that, if the vapour may be regarded as a perfect gas, the partial pressure $y_2 P_{\text{sat}}$ of the solute will be directly proportional to n_2. More generally, whether or not the vapour may be regarded as a perfect gas, the fugacity p_2 of 2 will be directly proportional to n_2, that is to say

$$p_2 \propto n_2. \qquad 5.06.1$$

This however raises the question whether the proportionality (1) holds at constant $n_1 + n_2$, that is to say

$$p_2 \propto x_2 \qquad 5.06.2$$

or at constant n_1, that is to say

$$p_2 \propto r_2. \qquad 5.06.3$$

The answer is that in the limit as x_2 and r_2 tend to zero (2) and (3) become equivalent and it is only in this limit that either is obviously true. At finite values of x_2 and r_2 we must not expect either (2) or (3) to be accurate, but we may use either as a basis for comparison with the actual behaviour of solutions. It is true that (2) can under favourable conditions hold for all values of x from 0 to 1 in which case we have an ideal mixture as described in §4.18. Formula (3) on the contrary becomes untenable as we approach the state of the pure liquid 2, when $r_2 \to 1$, since it would lead to the absurd conclusion that p_2^0 is infinite. We must however remember that in this chapter our convention that the species 1 is the solvent implies that this species is present in excess and we are consequently not concerned with conditions approaching that of the pure liquid 2. In fact we are concerned mainly with the condition $r_2 \ll 1$. Bearing in mind this implied restriction we are free to choose either (2) or (3) as a basis of comparison with actual behaviour.

In practice it has been found that (3) is more convenient than (2) because the value of r_2 is unaffected by the addition to a given solution of other solute species. This practical advantage will become clearer in the next chapter when we consider chemical reactions between solute species.

We shall accordingly choose as a basis of comparison with actual behaviour formula (3) after we have generalized it for several solute species when it becomes

$$p_s \propto r_s \qquad (T, P \text{ const.}). \qquad 5.06.4$$

It is clear from the relations in §4.12 that (4) is equivalent to

$$\lambda_s \propto r_s \qquad (T, P \text{ const.}) \qquad 5.06.5$$

and (5) is applicable to solute species of immeasurably low volatility. We shall now adopt (5) as our basis of comparison with actual behaviour and we define a solution as being *ideal dilute* when the proportionality (5) is obeyed for all values of r_s less than or equal to that of the solution under consideration.

We can write (5) in the alternative form

$$\lambda_s = \lambda_s^\infty r_s \qquad 5.06.6$$

where λ_s^∞ depends on the nature of the solute, the nature of the solvent, the temperature, and the pressure, but not on the mole ratio r_s of the solute considered nor on the mole ratio of any other solute species. In numerical applications, as opposed to general theory, it is customary to use molalities instead of mole ratios. We then replace (6) by

$$\lambda_s = \lambda_s^\ominus m_s \qquad 5.06.7$$

$$\lambda_s^\ominus = \lambda_s^\infty / r^\ominus \qquad 5.06.8$$

where $r^\ominus$ is defined by (5.02.1).

Finally we may, if we prefer, use chemical potentials instead of absolute activities. We then have in analogous notation

$$\mu_s = \mu_s^\infty + RT \ln r_s \qquad 5.06.9$$

$$\mu_s = \mu_s^\ominus + RT \ln m_s \qquad 5.06.10$$

$$\mu_s^\ominus = \mu_s^\infty - RT \ln r^\ominus. \qquad 5.06.11$$

§5.07 *Thermodynamic functions of ideal dilute solutions*

Having defined an ideal dilute solution in terms of the absolute activities or chemical potentials of the solute species, we can deduce the relations for the properties of the solvent by means of the Gibbs–Duhem relation (5.04.4)

$$\mathrm{d}\ln\lambda_1+\sum_s r_s\mathrm{d}\ln\lambda_s=0 \qquad (T, P \text{ const.}). \tag{5.07.1}$$

From (5.06.5) we have

$$r_s\mathrm{d}\ln\lambda_s=r_s\mathrm{d}\ln r_s=\mathrm{d}r_s \qquad (T, P \text{ const.}). \tag{5.07.2}$$

Substituting (2) into (1) we obtain

$$\mathrm{d}\ln\lambda_1=-\sum_s \mathrm{d}r_s=-\mathrm{d}(\sum_s r_s) \qquad (T, P \text{ const.}) \tag{5.07.3}$$

and so by integration

$$-\ln(\lambda_1/\lambda_1^0)=\sum_s r_s \qquad (T, P \text{ const.}) \tag{5.07.4}$$

where as usual the superscript ^{0} denotes the value for the pure liquid solvent. We can rewrite (4) in terms of chemical potentials

$$\mu_1=\mu_1^0-RT\sum_s r_s \qquad (T, P \text{ const.}) \tag{5.07.5}$$

and in terms of absolute activities

$$\ln\lambda_1=\ln\lambda_1^0-\sum_s r_s. \tag{5.07.6}$$

By use of (5.03.11) we deduce

$$V_1=V_1^0 \qquad (T, P \text{ const.}) \tag{5.07.7}$$

$$V_s=V_s^\infty \qquad (T, P \text{ const.}) \tag{5.07.8}$$

where V_s^∞ denotes the limiting value of V_s at infinite dilution of all solute species. We see then that V_1 and V_s are in an ideal dilute solution in a given solvent independent of the composition.

By use of (5.03.9) we deduce

$$S_1=S_1^0+R\sum_s r_s \qquad (T, P \text{ const.}) \tag{5.07.9}$$

$$S_s=S_s^\infty-R\ln r_s \qquad (T, P \text{ const.}) \tag{5.07.10}$$

where S_s^∞ is defined by

$$S_s^\infty=-\partial\mu_s^\infty/\partial T \tag{5.07.11}$$

and is thus in an ideal dilute solution in a given solvent independent of the composition.

By use of (5.03.10) we deduce

$$H_1=H_1^0 \tag{5.07.12}$$

$$H_s=H_s^\infty \tag{5.07.13}$$

where H_s^∞ denotes the limiting value of H_s at infinite dilution of all solute species.

It follows from (7), (8) and from (12), (13) that any two ideal dilute solutions in the same solvent mix at constant temperature and pressure without change of volume and without change of enthalpy.

§5.08 *Real solutions*

As already mentioned, we do not expect a real solution to be ideal dilute except in the limit of infinite dilution but it is convenient to compare the behaviour of any real solution with its hypothetical behaviour if it remained ideal dilute at all compositions extending from infinite dilution to its actual composition. We then express the deviations between the real behaviour and this hypothetical behaviour by means of certain coefficients as will be described in the succeeding sections.

§5.09 *Activity coefficients of solute species*

We define the activity coefficient γ_2 of the solute species 2 by the relations

$$\lambda_2=\lambda_2^\infty r_2\gamma_2=\lambda_2^\ominus m_2\gamma_2 \qquad (T, P \text{ const.}) \qquad 5.09.1$$

$$\gamma_2\to 1 \quad \text{as} \quad \sum_s m_s\to 0. \qquad 5.09.2$$

Alternatively we may express (1) in terms of chemical potentials

$$\mu_2=\mu_2^\infty+RT\ln(r_2\gamma_2)=\mu_2^\ominus+RT\ln(m_2\gamma_2) \qquad (T, P \text{ const.}) \quad 5.09.3$$

in conjunction with (2). It is clear that the deviation of γ_2 from unity or of $\ln\gamma_2$ from zero is a measure of deviation from an ideal dilute solution.

It need hardly be mentioned that similar relations hold for every solute species. Thus (1) may be generalized to

$$\lambda_s=\lambda_s^\infty r_s\gamma_s=\lambda_s^\ominus m_s\gamma_s \qquad (T, P \text{ const.}) \qquad 5.09.4$$

and (3) to

$$\mu_s=\mu_s^\infty+RT\ln(r_s\gamma_s)=\mu_s^\ominus+RT\ln(m_s\gamma_s) \qquad (T, P \text{ const.}). \quad 5.09.5$$

It is unfortunate that the same name *activity coefficient* is sometimes used for the quantity a/x of the previous chapter as well as for γ_s.

§5.10 *Osmotic coefficient of solvent*

Following Bjerrum* we define the osmotic coefficient ϕ of the solvent by

$$-\ln(\lambda_1/\lambda_1^0)=-\ln(p_1/p_1^0)=\phi\sum_s r_s \qquad (T,\,P\ \text{const.}). \qquad 5.10.1$$

By comparing (1) with (5.07.4) we see that $\phi-1$ is a measure of deviation of behaviour from that of an ideal dilute solution.

We can also write (1) in terms of chemical potentials as

$$\mu_1=\mu_1^0-RT\phi\sum_s r_s \qquad (T,\,P\ \text{const.}). \qquad 5.10.2$$

§5.11 *Relation between activity coefficients and osmotic coefficient*

When we substitute (5.10.1) and (5.09.4) into the Gibbs–Duhem relation (5.04.4) we obtain

$$\mathrm{d}(\phi\sum_s r_s)=\sum_s r_s\mathrm{d}\ln(r_s\gamma_s) \qquad (T,\,P\ \text{const.}) \qquad 5.11.1$$

which can be rewritten as

$$\mathrm{d}\{(\phi-1)\sum_s r_s\}=\sum_s r_s\mathrm{d}\ln\gamma_s \qquad (T,\,P\ \text{const.}) \qquad 5.11.2$$

a relation due to Bjerrum.† In the case of a single solute species (2) reduces to

$$\mathrm{d}\{(\phi-1)r\}/\mathrm{d}r=r\,\mathrm{d}\ln\gamma/\mathrm{d}r \qquad (T,\,P\ \text{const.}) \qquad 5.11.3$$

or

$$(\phi-1)/r+\mathrm{d}\phi/\mathrm{d}r=\mathrm{d}\ln\gamma/\mathrm{d}r \qquad (T,\,P\ \text{const.}). \qquad 5.11.4$$

If for example ϕ is related to r by

$$\phi-1=Ar^n \qquad (A,\,n\ \text{const.}) \qquad 5.11.5$$

then by substituting from (5) into (4) we obtain after integration

$$\ln\gamma=(1+n^{-1})Ar^n=(1+n^{-1})(\phi-1). \qquad 5.11.6$$

§5.12 *Temperature dependence*

By substitution of (5.09.4) into the second of equations (5.03.10) we obtain

$$\partial\ln\lambda_s^\infty/\partial T+\partial\ln\gamma_s/\partial T=-H_s/RT^2. \qquad 5.12.1$$

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* Bjerrum, Fysisk Tidskr. 1916 **15** 66; Z. Electrochem. 1918 **24** 325.

† Bjerrum, Z. Phys. Chem. 1923 **104** 406.

In the limit of infinite dilution (1) reduces to

$$\partial \ln \lambda_s^\infty/\partial T = -H_s^\infty/RT^2. \tag{5.12.2}$$

Subtracting (2) from (1) we obtain for the temperature dependence of the activity coefficient

$$\partial \ln \gamma_s/\partial T = -(H_s - H_s^\infty)/RT^2. \tag{5.12.3}$$

In particular we observe that γ_s will be independent of temperature if H_s is independent of composition.

By substitution of (5.10.1) into the first of equations (5.03.10) we obtain

$$-\sum_s r_s \partial\phi/\partial T + \partial \ln \lambda_1^0/\partial T = -H_1/RT^2. \tag{5.12.4}$$

For the pure solvent (4) reduces to

$$\partial \ln \lambda_1^0/\partial T = -H_1^0/RT^2. \tag{5.12.5}$$

By subtraction of (5) from (4) we find for the temperature dependence of the osmotic coefficient

$$\sum_s r_s \partial\phi/\partial T = (H_1 - H_1^0)/RT^2. \tag{5.12.6}$$

In particular we observe that ϕ will be independent of temperature if H_1 is independent of composition.

§5.13 *Pressure dependence*

By substitution of (5.09.5) into the second of equations (5.03.11) we obtain

$$\partial \mu_s^\infty/\partial P + RT\partial \ln \gamma_s/\partial P = V_s. \tag{5.13.1}$$

In the limit of infinite dilution (1) reduces to

$$\partial \mu_s^\infty/\partial P = V_s^\infty. \tag{5.13.2}$$

By subtraction of (2) from (1) we find for the pressure dependence of the activity coefficient

$$\partial \ln \gamma_s/\partial P = (V_s - V_s^\infty)/RT. \tag{5.13.3}$$

By substitution of (5.10.2) into the first of equations (5.03.11) we obtain

$$\partial \mu_1^0/\partial P - RT\sum_s r_s \partial\phi/\partial P = V_1. \tag{5.13.4}$$

For the pure solvent (4) reduces to

$$\partial \mu_1^0/\partial P = V_1^0. \tag{5.13.5}$$

By subtraction of (5) from (4) we obtain for the pressure dependence of the osmotic coefficient

$$\sum_s r_s \partial\phi/\partial P = -(V_1 - V_1^0)/RT. \qquad 5.13.6$$

All these pressure dependences are usually negligible at ordinary pressures.

§5.14 *Temperature dependence of fugacity of solvent*

From (5.10.1) we have

$$-\ln(p_1/p_1^0) = \phi \sum_s r_s. \qquad 5.14.1$$

Differentiating (1) with respect to T and using (5.12.6) we obtain for a solution of given composition

$$-\partial \ln(p_1/p_1^0)/\partial T = \sum_s r_s \partial\phi/\partial T = (H_1 - H_1^0)/RT^2. \qquad 5.14.2$$

§5.15 *Temperature dependence of fugacity of solute*

For a volatile solute species we may replace (5.09.4) by

$$p_s = p_s^\infty r_s \gamma_s = p_s^\ominus m_s \gamma_s \qquad 5.15.1$$

where p_s^∞, $p_s^\ominus$ are independent of the composition but depend on the nature of the solute s and the solvent. Differentiating (1) with respect to T and using (5.12.3) we obtain

$$-\partial \ln(p_s/p_s^\infty)/\partial T = -\partial \ln(p_s/p_s^\ominus)/\partial T = (H_s - H_s^\infty)/RT^2. \qquad 5.15.2$$

§5.16 *Osmotic pressure*

We recall formula (4.14.8)

$$\Pi\langle V_1\rangle/RT = \ln(p_1^0/p_1) \qquad 5.16.1$$

where $\langle V_1\rangle$ denotes the value of V_1 at a pressure equal to the mean of the pressure P on the pure solvent and the pressure $P+\Pi$ on the solution at osmotic equilibrium while both p_1 and p_1^0 are values at an external pressure P. Since formula (1) does not contain mole fractions it is equally applicable to solutions described in terms of mole ratios.

Substituting (5.10.1) into (1) we obtain

$$\Pi\langle V_1\rangle/RT = \phi \sum_s r_s. \qquad 5.16.2$$

If we use the superscript $^{\text{id}}$ to denote a hypothetical ideal dilute solution with the same composition as the actual solution we have

$$\Pi^{\mathrm{id}}\langle V_1\rangle/RT=\sum_s r_s. \qquad 5.16.3$$

Dividing (2) by (3) we find

$$\Pi=\phi\Pi^{\mathrm{id}} \qquad 5.16.4$$

and this relation explains the origin of the name *osmotic coefficient.*

§5.17 *Freezing point*

Let us now consider the equilibrium between the liquid solution and the pure solid solvent 1. We assume that the pressure is either constant or irrelevant. We use the superscript $^{\mathrm{S}}$ to denote the solid phase, the superscript ^{0} for the pure liquid, and no superscript for the liquid mixture. Then for equilibrium between the pure solid and the liquid mixture at its freezing point temperature T

$$\lambda_1(T)=\lambda_1^{\mathrm{S}}(T). \qquad 5.17.1$$

If T^0 denotes the corresponding equilibrium temperature for the pure liquid, that is to say the freezing point of the pure liquid, we have correspondingly

$$\lambda_1^0(T^0)=\lambda_1^{\mathrm{S}}(T^0). \qquad 5.17.2$$

Dividing (2) by (1) we obtain

$$\lambda_1^0(T^0)/\lambda_1(T)=\lambda_1^{\mathrm{S}}(T^0)/\lambda_1^{\mathrm{S}}(T) \qquad 5.17.3$$

which can be rewritten in the form

$$\lambda_1^0(T)/\lambda_1(T)=\{\lambda_1^0(T)/\lambda_1^0(T^0)\}/\{\lambda_1^{\mathrm{S}}(T)/\lambda_1^{\mathrm{S}}(T^0)\}. \qquad 5.17.4$$

Taking logarithms we have

$$\ln\{\lambda_1^0(T)/\lambda_1(T)\}=\ln\{\lambda_1^0(T)/\lambda_1^0(T^0)\}-\ln\{\lambda_1^{\mathrm{S}}(T)/\lambda_1^{\mathrm{S}}(T^0)\}. \qquad 5.17.5$$

Now applying the first relation (5.03.10)

$$\partial\ln\lambda_1/\partial T=-H_1/RT^2 \qquad 5.17.6$$

to the pure solid and pure liquid in turn and integrating we obtain

$$\ln\{\lambda_1^{\mathrm{S}}(T)/\lambda_1^{\mathrm{S}}(T^0)\}=-\int_{T^0}^{T}(H_1^{\mathrm{S}}/RT^2)\mathrm{d}T \qquad 5.17.7$$

$$\ln\{\lambda_1^0(T)/\lambda_1^0(T^0)\}=-\int_{T^0}^{T}(H_1^0/RT^2)\mathrm{d}T. \qquad 5.17.8$$

Substituting (7) and (8) into (5) we obtain

$$\ln\{\lambda_1^0(T)/\lambda_1(T)\}=-\int_{T^0}^{T}\{(H_1^0-H_1^{\mathrm{S}})/RT^2\}\mathrm{d}T=-\int_{T^0}^{T}(\Delta_{\mathrm{f}}H_1^0/RT^2)\mathrm{d}T \qquad 5.17.9$$

where $\Delta_f H_1^0$ is the proper enthalpy of fusion of the pure solvent. We now substitute (5.10.1) into (9) and obtain

$$\phi \sum_s r_s = -\int_{T^0}^{T} (\Delta_f H_1^0/RT^2)\mathrm{d}T \qquad 5.17.10$$

where ϕ denotes the osmotic coefficient of the solution at its freezing point.

We can rewrite (10) more simply as

$$\phi \sum_s r_s = \langle \Delta_f H_1^0 \rangle (1/RT - 1/RT^0) \qquad 5.17.11$$

where $\langle \Delta_f H_1^0 \rangle$ denotes the average value of $\Delta_f H_1^0$ over the reciprocal temperature interval $1/T^0$ to $1/T$. Since $\Delta_f H_1^0$ is always positive it follows that $T < T^0$. Thus the freezing point of the solution is always below that of the pure solvent if the solid phase is pure solvent.

For dilute solutions when $T^0 - T \ll T^0$ we may replace (11) by the approximation

$$\phi \sum_s r_s = \Delta_f H_1^0 (T^0 - T)/RT^{02} \qquad 5.17.12$$

or

$$T^0 - T = \phi \sum_s r_s (RT^{02}/\Delta_f H_1^0). \qquad 5.17.13$$

In numerical calculations it is customary to use the molalities m_s instead of the solute–solvent mole ratios r_s. We recall the definition (5.02.1) of molality

$$m_s = r_s/r^\ominus \qquad 5.17.14$$

where $r^\ominus$ is a standard value of r_s customarily chosen so that $r_s = r_s^\ominus$ when there is one mole of the solute s for each kilogramme of solvent. We accordingly rewrite (13) as

$$T^0 - T = \phi \sum_s m_s (r^\ominus RT^{02}/\Delta_f H_1^0). \qquad 5.17.15$$

The factor $r^\ominus RT^{02}/\Delta_f H_1^0$ which is a property of the solvent but common to all solute species, is called the *cryoscopic constant*. We note that when $r^\ominus$ is given the value $M_1/\text{kg mole}^{-1}$ then $\Delta_f H_1^0/r^\ominus$ is numerically equal to the enthalpy of fusion in joules per kilogramme of the solvent. For water we have

$$RT^0 = 2.2712 \times 10^3 \text{ J mole}^{-1}$$
$$T^0 = 273.15 \text{ K}$$
$$\Delta_f H_1^0/r^\ominus = 3.335 \times 10^5 \text{ J mole}^{-1}$$

so that the cryoscopic constant is

$$2.2712 \times 10^3 \text{ J mole}^{-1} \times 273.15 \text{ K}/3.335 \times 10^5 \text{ J mole}^{-1} = 1.860 \text{ K}. \qquad 5.17.16$$

§5.18 *Boiling point*

We shall now consider the equilibrium between the liquid solution and the gas phase in the case that all the solute species have negligible vapour pressures. We accordingly regard the gas phase as consisting entirely of the component 1 and we use the superscript $^{\mathrm{G}}$ to denote this phase.

We then proceed to consider the equilibrium between the two phases at a given pressure precisely as in the case of equilibrium with a pure solid phase studied in the previous section. The steps of the argument are precisely analogous and we obtain eventually the relation

$$\phi \sum_s r_s = \langle \Delta_e H_1^0 \rangle (1/RT^0 - 1/RT) \qquad 5.18.1$$

where $\langle \Delta_e H_1^0 \rangle$ denotes the value of the proper enthalpy of evaporation $\Delta_e H_1^0$ for the pure liquid averaged over the reciprocal temperature interval $1/T$ to $1/T^0$ and ϕ is the osmotic coefficient at the boiling point of the solution. Since $\Delta_e H_1^0$ is always positive it follows that $T > T^0$. Thus the boiling point of any solution of non-volatile solutes is above that of the pure solvent.

For dilute solutions when $T - T^0 \ll T^0$ we may replace (1) by the approximation

$$\phi \sum_s r_s = \Delta_e H_1^0 (T - T^0)/RT^{02} \qquad 5.18.2$$

or

$$T - T^0 = \phi \sum_s r_s (RT^{02}/\Delta_e H_1^0). \qquad 5.18.3$$

For purposes of numerical calculation it is customary to use the molalities m_s instead of the solute–solvent mole ratios r_s. We accordingly rewrite (3) as

$$T - T^0 = \phi \sum_s m_s (r^{\ominus} RT^{02}/\Delta_e H_1^0). \qquad 5.18.4$$

The factor $r^{\ominus} RT^{02}/\Delta_e H_1^0$ is called the *ebullioscopic constant* of the solvent. We note that when $r^{\ominus}$ is as usual chosen to be M_1 mole kg^{-1} then $\Delta_e H_1^0/r^{\ominus}$ is numerically equal to the enthalpy of evaporation in joules per kilogramme of solvent. For water we have

$$RT^0 = 3.1026 \times 10^3 \text{ J mole}^{-1}$$
$$T^0 = 373.15 \text{ K}$$
$$\Delta_e H_1^0/r^{\ominus} = 2.2567 \times 10^6 \text{ J mole}^{-1}$$

so that the ebullioscopic constant is

$$3.1026 \times 10^3 \text{ J mole}^{-1} \times 373.15 \text{ K}/2.2567 \times 10^6 \text{ J mole}^{-1} = 0.513 \text{ K}. \qquad 5.18.5$$

§5.19 *Distribution between two solvents*

For the equilibrium of a solute species s between two solutions in different solvents we have

$$\lambda_s^{\alpha} = \lambda_s^{\beta} \qquad 5.19.1$$

where the superscripts $^{\alpha}$ and $^{\beta}$ relate to the two phases. Substituting from (5.09.4) into (1) we obtain

$$\lambda_s^{\ominus\alpha} m_s^{\alpha} \gamma_s^{\alpha} = \lambda_s^{\ominus\beta} m_s^{\beta} \gamma_s^{\beta} \qquad 5.19.2$$

or by rearrangement

$$m_s^{\beta} \gamma_s^{\beta} / m_s^{\alpha} \gamma_s^{\alpha} = l_s^{\alpha\beta} \qquad 5.19.3$$

where $l_s^{\alpha\beta}$ is independent of the composition of the two phases and is defined by

$$l_s^{\alpha\beta} = \lambda_s^{\ominus\alpha} / \lambda_s^{\ominus\beta}. \qquad 5.19.4$$

In the special case that both solutions are ideal dilute (3) reduces to

$$m_s^{\beta} / m_s^{\alpha} = l_s^{\alpha\beta} \qquad 5.19.5$$

which is known as *Nernst's distribution law.*

§5.20 *Solubility of pure solid*

For the equilibrium with respect to the species s between a solution and the pure solid phase we have the condition

$$\lambda_s = \lambda_s^{\mathrm{S}} \qquad 5.20.1$$

where the superscript $^{\mathrm{S}}$ denotes the pure solid phase. Substituting from (5.09.4) into (1) we obtain

$$m_s \gamma_s = \lambda_s^{\mathrm{S}} / \lambda_s^{\ominus} \qquad \text{(saturated solution).} \qquad 5.20.2$$

From (2) we see that if several solutions in the same solvent at the same temperature are all saturated with the same solid phase of the species s, then in all these solutions $m_s \gamma_s$ has the same value.

Taking logarithms of (2), differentiating with respect to T and using (5.12.3) we obtain

$$\partial \ln(m_s \gamma_s) / \partial T = (H_s^{\infty} - H_s^{\mathrm{S}}) / RT^2 \qquad \text{(saturated solution)} \qquad 5.20.3$$

and we observe that the quantity $H_s^{\infty} - H_s^{\mathrm{S}}$ occurring as the numerator on the right is the *proper enthalpy of dissolution* of s at infinite dilution.

§5.21 *Experimental determination of ϕ*

The most accurate direct method of determining ϕ experimentally is by measurements of freezing point and use of formula (5.17.11) which for a single solute species reduces to

$$\phi m_s = \phi r_s/r^{\ominus} = (T^0 - T)(\langle \Delta_f H_1^0 \rangle / r^{\ominus} R T^0 T). \qquad 5.21.1$$

All the quantities m_s, $\Delta_f H_1^0$, T^0, T can be measured and substitution of their values into (1) leads to experimental values of ϕ at the freezing point.

Let us suppose that freezing-point measurements have been made so as to determine ϕ over a range of steadily decreasing values of m and let us consider what results are to be expected.

Since we know that as $m \rightarrow 0$ so $\phi \rightarrow 1$ we may reasonably expect that $\phi - 1$ can be expressed as a series of integral powers of m say

$$\phi - 1 = A_1 m + A_2 m^2 + \ldots. \qquad 5.21.2$$

This is in fact the case for non-electrolytes and we may then hope to determine by a series of accurate freezing-point measurements the coefficients in such a formula as (2) so as to obtain a good fit. Formula (2) is not applicable to solutions of electrolytes; these will be discussed in chapter 7.

Let us now consider what will happen if the measurements are extended down to gradually decreasing values of m. If the measurements are performed with sufficient care, we may expect to reach a range where all terms of (2) are negligible except the first. In this range $(\phi - 1)/m$ has a constant value A_1 and we may confidently and reasonably assume that this behaviour persists down to $m = 0$. Suppose however we tried to confirm this experimentally, let us examine what would happen.

We may reasonably assume that the experimental error in measuring $T^0 - T$ is at least roughly independent of m. Since at low values of m the value of $T^0 - T$ is itself roughly proportional to m it follows that the fractional experimental error in ϕ is inversely proportional to m. Hence according to (2) the fractional error in $\phi - 1$ will be inversely proportional to m^2. It is therefore clear that by proceeding to experiment at smaller values of m we eventually reach a stage where the experiments tell us nothing.

The most reasonable procedure is then to carry the experiments down to values of m where one finds experimentally

$$(\phi - 1)/m = A_1 \qquad (A_1 \text{ const.}) \qquad 5.21.3$$

and then assume that this simple law persists down to $m = 0$.

We may mention that for solutions of non-electrolytes the limiting law

(3) has not merely an empirical basis, but also a theoretical one based on statistical mechanics.

§5.22 *Determination of γ from ϕ*

We recall Bjerrum's relation for a single solute species (5.11.3)

$$\mathrm{d}\{(\phi-1)r\}/\mathrm{d}r = r\,\mathrm{d}\ln\gamma/\mathrm{d}r \qquad (T, P \text{ const.}) \qquad 5.22.1$$

which we may also write as

$$\mathrm{d}\{(\phi-1)m\}/\mathrm{d}m = m\,\mathrm{d}\ln\gamma/\mathrm{d}m \qquad (T, P \text{ const.}) \qquad 5.22.2$$

or as

$$\mathrm{d}\ln\gamma = [\mathrm{d}\{(\phi-1)m\}/\mathrm{d}m]\,\mathrm{d}\ln m \qquad (T, P \text{ const.}). \qquad 5.22.3$$

Integrating (3) from 0 to m and observing that $\phi-1$ and $\ln\gamma$ tend to zero as m tends to zero, we obtain

$$\ln\gamma = \int_0^m [\mathrm{d}\{(\phi-1)m\}/\mathrm{d}m]\,\mathrm{d}\ln m = \phi-1+\int_0^m (\phi-1)\,\mathrm{d}\ln m. \qquad 5.22.4$$

If ϕ has been determined at all molalities from 0 to m we see that by using (4) we can in principle calculate γ at a molality m but caution is required so as to avoid spurious results. We saw in the previous section that with regard to the experimental determination of ϕ there are three ranges of m arranged in order of decreasing m with the following characteristics.

1. Large molalities, where ϕ can be measured and fitted to a more or less complicated formula.
2. Intermediate molalities, where ϕ can be fitted to the formula

$$\phi-1 = A_1 m \qquad (A_1 \text{ const.}). \qquad 5.22.5$$

3. Lowest molalities, where no useful information about ϕ can be obtained by experiment and we assume that (5) continues to hold.

In using (4) it is expedient to break the range of integration at some value m' of m in the range where (5) is found to hold. We accordingly rewrite (4) as

$$\ln\gamma = \phi-1+\int_0^{m'} (\phi-1)\,\mathrm{d}\ln m + \int_{m'}^{m} (\phi-1)\,\mathrm{d}\ln m. \qquad 5.22.6$$

We evaluate the first integral as follows

$$\int_0^{m'} (\phi-1)\,\mathrm{d}\ln m = \int_0^{m'} A_1\,\mathrm{d}m = A_1 m' = \phi'-1 \qquad 5.22.7$$

where ϕ' denotes the value of ϕ at $m=m'$. Using (7) in (6) we obtain finally

$$\ln \gamma=\phi-1+\phi'-1+\int_{m'}^{m}(\phi-1)\,\mathrm{d}\ln m \qquad 5.22.8$$

and the integral in (8) can be evaluated from the experimental values of ϕ, either by fitting these to a formula or graphically.

The important point emerging from this discussion is that we cannot calculate γ from experimental determinations of ϕ for example by freezing-point measurements, without making an assumption concerning ϕ at low values of m. Since such an assumption has to be made anyway, it is just as well to make it explicitly and so obtain a closed formula for γ as well as for ϕ in the range of small m. For solutions of non-electrolytes, with which we are here concerned, the usual and most reasonable assumption is formula (5). In chapter 7, when we study solutions of electrolytes, we shall meet a different situation.

§5.23 *Fugacity of saturated solution*

Throughout this chapter and the previous one we have never yet considered any equilibrium involving more than two bulk phases, nor shall we do so in any detail. No new principles are involved and the methods already described are applicable. We shall confine ourselves to a single interesting example.

We consider the following problem. How does the fugacity of the solvent vary with the temperature in a solution kept saturated with a single non-volatile solid? Using the subscripts $_1$ for the solvent, $_2$ for the solute, and the superscripts $^{\mathrm{G}}$ for the gas phase, $^{\mathrm{S}}$ for the solid, and none for the solution, we have for variations maintaining equilibrium

$$\mathrm{d}\ln \lambda_1=\mathrm{d}\ln \lambda_1^{\mathrm{G}} \qquad 5.23.1$$

$$\mathrm{d}\ln \lambda_2=\mathrm{d}\ln \lambda_2^{\mathrm{S}}. \qquad 5.23.2$$

Expanding these, and neglecting the effect of pressure on each of the condensed phases we have

$$-(H_1/RT^2)\mathrm{d}T+(\partial \ln \lambda_1/\partial m_2)\mathrm{d}m_2=-(H_1^{\mathrm{G}}/RT^2)\mathrm{d}T+\mathrm{d}\ln p_1 \qquad 5.23.3$$

$$-(H_2/RT^2)\mathrm{d}T+(\partial \ln \lambda_2/\partial m_2)\mathrm{d}m_2=-(H_2^{\mathrm{S}}/RT^2)\mathrm{d}T. \qquad 5.23.4$$

Using $\Delta_{\mathrm{e}}H$ to denote the proper enthalpy of evaporation from the solution and $\Delta_{\mathrm{f}}H$ to denote the proper enthalpy of fusion into the solution, we can write (3) and (4) as

$$\mathrm{d}\ln p_1=(\partial \ln \lambda_1/\partial m_2)\mathrm{d}m_2+(\Delta_{\mathrm{e}}H_1/RT^2)\mathrm{d}T \qquad 5.23.5$$

$$(\partial \ln \lambda_2/\partial m_2)\mathrm{d}m_2=(\Delta_{\mathrm{f}}H_2/RT^2)\mathrm{d}T. \qquad 5.23.6$$

We now use the Gibbs–Duhem relation in the form

$$\partial \ln \lambda_1/\partial m_2 + r(\partial \ln \lambda_2/\partial m_2) = 0 \qquad 5.23.7$$

to eliminate λ_1, λ_2 from (5), (6). We thus obtain

$$\mathrm{d} \ln p_1/\mathrm{d}T = (\Delta_e H_1 - r\Delta_f H_2)/RT^2. \qquad 5.23.8$$

It is interesting to observe that the expression inside the brackets is equal and opposite to the *enthalpy of formation* of the quantity of solution containing unit amount of solvent from the gaseous solvent and from the solid solute.

§5.24 *Surface tension*

We conclude this chapter with a brief discussion of interfacial layers, particularly those between a liquid and its vapour. As described in §4.36 we shall neglect effects of pressure on the liquid phase and on the surface layer.

For the sake of brevity we use the symbol D to denote the operator $\Sigma_s \mathrm{d}r_s \partial/\partial r_s$. We have then by analogy with (4.36.4), (4.36.5), and (4.36.6)

$$-\mathrm{d}\gamma = S_A^\sigma \mathrm{d}T + \Gamma_1 \mathrm{d}\mu_1 + \sum_s \Gamma_s \mathrm{d}\mu_s \qquad 5.24.1$$

$$\mathrm{d}\mu_1 = -S_1 \mathrm{d}T + \mathrm{D}\mu_1 \qquad 5.24.2$$

$$\mathrm{d}\mu_s = -S_s \mathrm{d}T + \mathrm{D}\mu_s \qquad 5.24.3$$

where (2) and (3) relate to the liquid phase*. We also have in the liquid phase the Gibbs–Duhem relation (5.04.3)

$$\mathrm{D}\mu_1 + \sum_s r_s \mathrm{D}\mu_s = 0. \qquad 5.24.4$$

Substituting (2) and (3) into (1) we obtain

$$-\mathrm{d}\gamma = (S_A^\sigma - \Gamma_1 S_1 - \sum_s \Gamma_s S_s)\mathrm{d}T + \Gamma_1 \mathrm{D}\mu_1 + \sum_s \Gamma_s \mathrm{D}\mu_s. \qquad 5.24.5$$

Now eliminating $\mathrm{D}\mu_1$ between (4) and (5) we obtain finally

$$-\mathrm{d}\gamma = (S_A^\sigma - \Gamma_1 S_1 - \sum_s \Gamma_s S_s)\mathrm{d}T + \sum_s (\Gamma_s - r_s \Gamma_1)\mathrm{D}\mu_s. \qquad 5.24.6$$

By reasoning similar to that of §4.37 we can verify the invariance of the coefficients of $\mathrm{d}T$ and $\mathrm{D}\mu_s$ with respect to shifts of the geometrical surfaces bounding the surface layer.

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* There should be no confusion between γ denoting surface tension and the activity coefficients γ_s.

§5.25 *Temperature dependence*

For the temperature dependence of the surface tension at constant composition of the liquid we obtain immediately from (5.24.6)

$$-\mathrm{d}\gamma/\mathrm{d}T = S_A^\sigma - \Gamma_1 S_1 - \sum_s \Gamma_s S_s \qquad 5.25.1$$

where the right side is the entropy of unit area of the surface layer less the entropy of the same material content in the liquid phase.

By proceeding as in §4.38 we can transform (1) to the equivalent relation

$$\gamma - T\,\partial\gamma/\partial T = U_A^\sigma - \Gamma_1 U_1 - \sum_s \Gamma_s U_s. \qquad 5.25.2$$

The right side is the energy which must be supplied to prevent any change of temperature when unit area of surface is formed from the liquid.

§5.26 *Variations of composition*

For variations of composition at constant temperature (5.24.6) reduces to

$$-\mathrm{d}\gamma = \sum_s (\Gamma_s - r_s\Gamma_1)\mathrm{D}\mu_s \qquad 5.26.1$$

or using

$$\mathrm{D}\mu_s = RT\,\mathrm{D}\ln\lambda_s = RT\,\mathrm{D}\ln p_s \qquad 5.26.2$$

$$-\mathrm{d}\gamma = RT\sum_s (\Gamma_s - r_s\Gamma_1)\mathrm{D}\ln p_s. \qquad 5.26.3$$

Each of the quantities

$$\Gamma_s - r_s\Gamma_1 \qquad 5.26.4$$

occurring on the right side of (3) is called the *surface excess* per unit area of the solute species s. The corresponding quantity for the solvent species 1 vanishes by definition. As we have repeatedly stressed, each quantity (4), in contrast to the individual Γ's is invariant with respect to shift of the boundary between the liquid phase and the surface phase and is therefore physically significant. The quantities (4) are the same as the quantities which Gibbs* denoted by $\Gamma_{s(1)}$ but his definition of these quantities was more abstract and more difficult to visualize.

§5.27 *Interfacial tension between two solutions*

For the interface between two liquid phases α, β neglecting dependence on

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* Gibbs, Collected Works, Longmans, vol. **1** pp. 234–235.

pressure, we have

$$-\mathrm{d}\gamma = S_A^\sigma \mathrm{d}T + \Gamma_1 \mathrm{d}\mu_1 + \sum_s \Gamma_s \mathrm{d}\mu_s. \qquad 5.27.1$$

The Gibbs–Duhem relation for phase α can be written

$$(1 + \sum_s r_s^\alpha) S_\mathrm{m}^\alpha \mathrm{d}T + \mathrm{d}\mu_1 + \sum_s r_s^\alpha \mathrm{d}\mu_s = 0 \qquad 5.27.2$$

and that for phase β

$$(1 + \sum_s r_s^\beta) S_\mathrm{m}^\beta \mathrm{d}T + \mathrm{d}\mu_1 + \sum_s r_s^\beta \mathrm{d}\mu_s = 0. \qquad 5.27.3$$

If there are $c-1$ solute species, there are $c+1$ quantities $\mathrm{d}T$, $\mathrm{d}\mu_1$, $\mathrm{d}\mu_s$ in (1) of which any two can be eliminated by using (2) and (3). The results obtainable are complicated and we shall not pursue them here.

§5.28 *Volume concentrations*

In analytical work it has long been the usual practice to describe the composition of a solution by the *volume concentration* c_s of each solute species defined as

$$c_s = n_s/V = r_s n_1/V. \qquad 5.28.1$$

As long as we are concerned with the properties of the solution at only one temperature this practice is unobjectionable. But in thermodynamics we are much interested in the temperature dependence of properties, and volume concentrations are then inconvenient. For whatever quantities be used to describe the composition of a liquid solution, it is expedient to use as the other two independent variables temperature and pressure, so that differentiation with respect to temperature implies constant pressure. We therefore have

$$\partial c_s/\partial T = -\alpha c_s \qquad 5.28.2$$

where α is the thermal expansivity. It is evident from (2) that, if c_s is chosen as a variable, it will not be an independent variable. On these grounds volume concentrations are not convenient in liquid solutions and we shall not use them.

Volume concentrations of course play an important part in the theory of gas kinetics. The implication, sometimes met, that they must therefore play a parallel part in the theory of solution kinetics shows a lack of appreciation of the utterly different and much more complex meaning of the word *collision* applied to a solution in contrast to a gas. We have not yet a complete theoretical treatment of collisions in solution, but the author believes that a successful theory would be based on molecular ratios rather than on volume concentrations.