Chapter 13

Determination of the Activity of the Nonelectrolytes

Abstract The most used methods of determination of the activities of the nonelectrolytes are mentioned in this chapter. In addition, they may also be applied to solutions of electrolytes. This aspect will be studied in the next one. At its beginning, the principle of the determination of an activity of one component from that of the other component of a binary solution is recalled. It is founded on the Gibbs–Duhem's relation. The mentioned methods are those based on the determination:

Of vapor pressures
Of the activity of the solvent from the determination of its freezing point
Of the osmotic pressure
Of electromotive forces of suitable electrochemical cells
From gas chromatography
From excess functions and empirical relations

Values of some activities of this kind of solutes are given in this chapter. The very important fact to know is the following one: the determination of the activities of nonelectrolytes is a possible task.

Keywords Henry's law • Gibbs–Duhem relation • Activity of one compound from that of the other • Freezing point depression • Electrochemical cell • Gas chromatography • Excess function

In this chapter, we mention the most used methods of determination of the activities of the nonelectrolytes. In addition, they may also be applied to solutions of electrolytes. This aspect will be studied in the next chapter. After having recalled the principles of these methods, we shall give some results and values of some activities of this kind of solutes.

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13.1 Activity of One of the Components of a Binary Solution from That of the Other Component

Once the activity of a component of a binary solution, solvent, or solute is determined, it is possible to calculate the activity of the other component starting from the value of the former. The calculation is founded on the Gibbs–Duhem's relation, one form of which is (viz. Chap. 5)

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

Given the definition of an activity from the chemical potential

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

the Gibbs–Duhem's relation becomes

$$x_1 d\ln a_1 + a_2 d \ln a_2 = 0 \tag{13.1}$$

This expression is applicable at constant pressure and temperature whatever the adopted standard states since the chemical potential of a species in a given state is constant for a given temperature. The rearranged relation (13.1) is

$$d\ln a_1 = -(x_2/x_1) d \ln a_2 \tag{13.2}$$

$$d\ln a_2 = -(x_1/x_2) d \ln a_1 \tag{13.3}$$

13.1.1 Activity of the Solvent from That of the Solute

The integration of relation (13.2) gives

$$\ln\left(a_1/a_1'\right) = -\int_{x_2'}^{x_2} (x_2/x_1) d \ln a_2 \tag{13.4}$$

a_1 and a_1' are the activities of the solvent in the two solutions where the molar fractions of the solute are x_2 and x_2'. The ratio a_1/a_1' is calculated by drawing the curve (x_2/x_1) in ordinates as a function of the values ln a_2 in abscissas and by determining the area under the curve between the limits x_2' and x_2.

Actually, this process is poorly convenient from the standpoint of the precision of the results. since, when the solution is very dilute, ln a_2 exhibits very large negative values and, as a result, the evaluation of the area under the curve is not precise. It is based on expression (13.5) below, similar to (13.4). An interesting variant of this integration process has been proposed.

It involves the activity coefficients rather than the activities themselves. Its principle stems from the following reasoning. For a binary solution:

$$x_1 + x_2 = 1$$

$$dx_1 + dx_2 = 0$$

$$x_1(dx_1/x_1) + x_2(dx_{2/}x_2) = 0$$

$$x_1 d \ln x_1 + x_2 d \ln x_2 = 0$$

Subtracting this expression from (13.1), we obtain

$$d \ln(a_1/x_1) = -(x_2/x_1) d \ln(a_1/x_2)$$

and after integration

$$\ln(a_1/x_1) - \ln(a_1'/x_1') = -\int_{x1}^{x2} (x_2/x_1) d \ln(a_2/x_2) \tag{13.5}$$

This relation can be simplified. At infinite dilution, $x_1' = 1$ and $x_2' = 0$; the activity a_1' of the solvent is equal to unity because of the choice of the standard state usually done (the unity of "concentration" is the molar fraction). The second term of the left member vanishes and we obtain

$$\ln(a_1/x_1) = -\int_{0}^{x2} (x_2/x_1) d \ln(a_2/x_2) \tag{13.6}$$

The area under the curve limited by the values $x_2 = 0$ and x_2 gives the value $\ln \gamma_1$ at the concentration x_2.

As examples, Table 13.1 provides the necessary experimental data in order to calculate the activity of mercury in the case of the amalgam of thallium at 20 °C. They are stemming from the electromotive force of appropriate electrochemical cells (viz. paragraph 5). In this table, x_2 is the molar fraction of thallium, a_2 its activity, and a_1 the activity of mercury being searched for.

Table 13.1 Activity coefficients of mercury in some amalgams by applying relation (13.6) (According to G.N. Lewis and M. Randall: Thermodynamics and the free energy of chemical substances: McGraw-Hill company, Inc, New York, 1923)

x_2	x_2/x_1	a_2/x_2	a_1/x_1
0	0	1	1
0.005	0.00502	1.06	0.9998
0.01	0.0101	1.15	0.999
0.05	0.0526	1.80	0.986
0.1	0.111	2.84	0.950
0.2	0.250	4.98	0.866
0.3	0.428	6.60	0.790
0.4	0.667	7.57	0.734
0.5	1.000	7.98	0.704

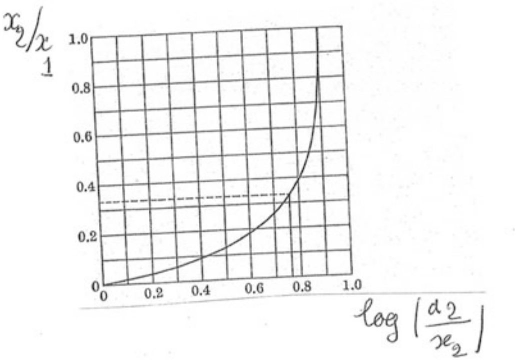

Fig. 13.1 Example of curve $(x_2/x_1)/\log(a_2/x_2)$ permitting the obtention of the activity of the solvent as the function of that of the solute (case of thallium amalgams) (viz. Table 13.1 and paragraph 5)

Figure 13.1 shows the corresponding curve $(x_2/x_1)/\log(a_2/x_2)$, the appropriate area determination of which permitting the calculation of the activity coefficients a_1/x_1.

13.1.2 Activity of the Solute as a Function of That of the Solvent

The determination is based on relation (13.3) or on the following one:

$$d\ln(a_2/x_2) = -(x_1/x_2)d\ln(a_1/x_1)$$

or

$$\ln(a_2/x_2) = -\int_0^{x_2}(x_1/x_2)d\ln(a_1/x_1) \tag{13.7}$$

Table 13.2 mentions the experimental data necessary to calculate the activity of thallium from the activity values a_1 of mercury in a thallium amalgam, through relation (13.7) (determination at 325 °C).

The curve $(x_1/x_2)/\log(a_1/x_1)$ built with the values of Table 13.2 is presented in Fig. 13.2. (The indexes 1 and 2 remain affected, respectively, to mercury and thallium.)

Actually, the graphical integration of (13.7) is difficult since for the solutions very dilute (in solute), the ratio x_1/x_2 tends toward infinite. Hence, this process entails to possess very precise data at high dilutions. (Among others, there exists a means to overcome this problem by a process of graphical extrapolation. Another consists in carrying out a fit of an algebraic function on some experimental points which are not endowed with a great imprecision.)

Table 13.2 Activity coefficients of mercury in some amalgams by applying relation (13.7) (According to G.N. Lewis and M. Randall: Thermodynamics and the free energy of chemical substances: McGraw-Hill Company, Inc, New York, 1923)

x_2	$\frac{a_1}{x_1}$	$\frac{a_2}{x_2}$
0	1	1
0.10	0.98	1.53
0.20	0.95	1.86
0.30	0.92	2.05
0.40	0.80	2.17
0.50	0.87	2.23
0.60	0.85	2.28
0.70	0.83	2.30
0.80	0.82	2.31
(1.00)	(0.80)	(2.32)

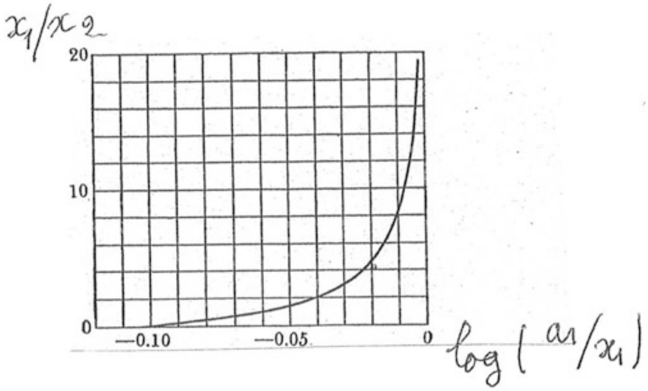

Fig. 13.2 Example of curve $x_1/x_2/\log(a_1/x_1)$ permitting the calculation of the thallium activity in some amalgams

13.2 Determination by Measurements of Vapor Pressures

Given the fact that the activity of every component of a solution is equal to the ratio of its fugacity in the studied state and of its fugacity in the standard state and given the links existing between the fugacity and the vapor pressure, it is intuitive that measurements of partial pressure vapors may permit to approach the values of the activities. The first condition is that the partial pressure vapor must be sufficiently large in order to be measurable. However, it must not be too large in order to be assimilated to its fugacity. That is to say, its partial pressure must obey the perfect gas law. In these conditions

$$a = f/f^\circ$$

$$a \approx p/p^\circ$$

According to these considerations, we can determine the activity either of the solvent or of the solute.

13.2.1 Activity of the Solvent a_1

The method of determination is based on the relation

$$a_1 \approx p_1/p_1{}^{\circ}$$

p_1 is the vapor pressure of the solvent in equilibrium with the solution where its activity is a_1. $p_1{}^{\bullet}$ is its vapor pressure in the standard state. The effect of the external pressure may be considered as being negligible. Let us recall (viz. Chap. 11) that the standard state of the solvent is unanimously chosen is the pure solvent at the temperature and pressure of the system. Then, we can write

$$a_1 \approx p_1/p_1{}^{\bullet}$$

$p_1{}^{\bullet}$ is the vapor pressure in the pure state at the same temperature and approximately at the same pressure as the solution.

This method of determination of the activities of the solvents has been used for aqueous and organic solutions.

13.2.2 Activity of the Solute a_2

If the solute is sufficiently volatile in such a manner that the determination of its vapor pressure above its solution is possible, its activity can be determined in the same conditions as above through the measurement of its vapor pressure p_2 in the state of the system and in the standard state $p_2{}^{\circ}$ through the relation

$$a_2 = p_2/p_2{}^{\circ}$$

$\mathbf{p}_2{}^{\circ}$ is not, usually, the vapor pressure of the pure solute. $\mathbf{p}_2{}^{\circ}$ is the vapor pressure which would be exhibited by the solute in the hypothetical standard state consisting in a molal solution where it would obey Henry's law. We have seen (viz. Chap. 11) that

$$p_2{}^{\circ} = k_{\mathrm{H}}$$

The fugacity and, hence, the vapor pressure of the solute in the standard state are equal to the constant k_{H} of Henry's law in the conditions mentioned above.

We know that in order to determine the latter, we linearly extrapolate the Henry's law until the molality unity.

From a practical standpoint, it may happen that the value of the vapor pressure appreciably deviates from a line as soon as the molalities are very weak. In this case, we must use another process to determine the constant k_{H}. It is also a graphical one. It consists in drawing the diagram solute pressure p_2 as a function of its

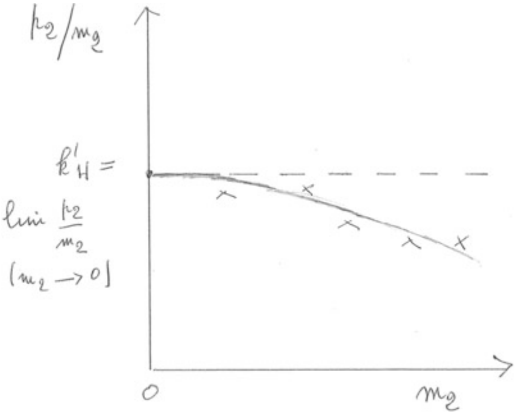

Fig. 13.3 Graphical determination of the partial pressure of the solute in its standard state

molality m_2. The obtained curve is extrapolated until down to the molality m_2 null—Fig. 13.3.

At null molality, the ratio p_2/m_2 is equal to the Henry's constant, that is to say, to the fugacity in the standard state. At null molality, indeed

$$p_2 \rightarrow f_2 \quad \text{and} \quad a_2 \rightarrow m$$

As a result

$$(p_2{}^{\circ}/m)_{m=0} = f_2/a_2$$

and since $a_2 = f_2/f_2{}^{\circ}$

$$(p_2{}^{\circ}/m)_{m=0} = f_2{}^{\circ}$$
$$(p_2{}^{\circ}/m)_{m=0} = k_{\mathrm{H}}$$

Graphical processes may also be used when the "concentration" scales to which are related the activities are those of molarities and of molar fractions. Molalities are simply replaced by the molar fractions and molarities in the drawing of diagrams.

Another approach is possible, but it is more rarely used than the previous one because of the fact that it is only practised when the solvent and the solute are essentially miscible in the whole range of concentrations. Then, for the standard state of the solute, one can choose it in its pure state. Then, we are again in the case in which it remains to determine the activity of the solvent. In this new standard state, the vapor pressure of the solute is roughly equal to its vapor pressure in the pure state. An interesting example of this double possibility of choice of a convenient standard state is provided by the solutions of dibromine in carbon tetrachloride. The diagram of the vapor pressure p_2 of dibromine as a function of its molar fraction is shown in Fig. 13.4.

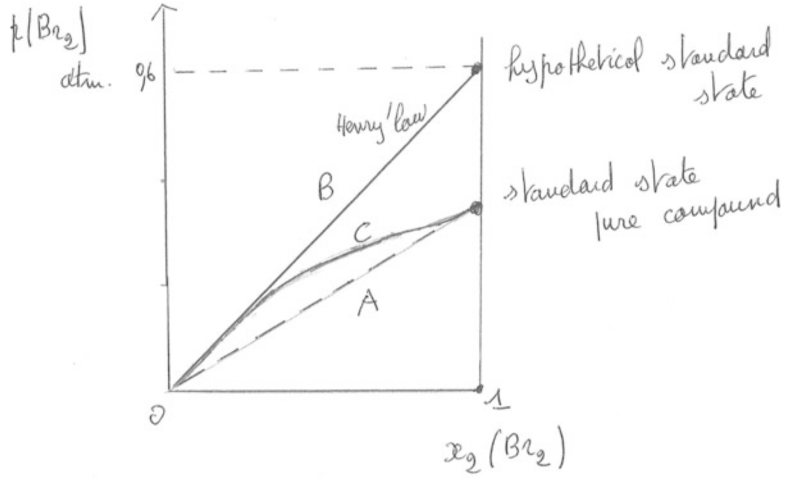

Fig. 13.4 Vapor pressure of dibromine as a function of its molar fraction in a solution of carbon tetrachloride (According to G.N. Lewis and M. Randall: Thermodynamics and the free energy of chemical substances: McGraw-Hill company, Inc, New York, 1923)

The line B is that of Henry. The pressure of bromine in this hypothetical standard state is 0.539 atm. The line A shows the calculated values of the pressure if the solution was perfect, the pure dibromine exhibiting a value of 0.280 atm. Hence, it is the pressure in the real standard state defined as being the pure compound. The curve C is the experimental one. The fugacity of the dibromine at each molar fraction being equal to its vapor pressure p_2 whatever the chosen standard state, it is evident that both activities according to the two standard states ax_2 (Henry) and ax_2 (real) are in the ratio

$$a_{x_2}(\text{Henry})/a_{x2}(\text{real}) = 0.280/0.539$$

This is an excellent illustration of the fact that in the same thermodynamic state, the activity of a compound may exhibit different values according to the adopted standard state.

13.3 Activity of the Solvent from the Determination of Its Freezing Point

This process is very general. Although it is, in principle, a method of determination of the activity of the solvent, it also permits to obtain that of the solute in the case of the binary solution. Then, the activity of the solute is determined through the use of the Gibbs–Duhem's relation once the activity of the solvent is known (viz. paragraph 1 above). In this chapter, essentially we set up a general relation between the solvent activity and the depression of the freezing point. Supplementary precisions will be given in the next chapter devoted to the determination of the activities of electrolytes.

13.3.1 General Considerations

The matter of the whole paragraph is the depression of the freezing point of the solvent of a binary dilute solution. The phenomenon is a consequence of the equilibrium solid–liquid.

When a solid is separating from a binary solution, three cases may exist according to the nature of the solid phase. The latter can be constituted by:

- The pure solute: In this case, the composition of the solution is purely and simply the solubility of the solute at the pressure and temperature of the system.
- The pure solvent: The temperature of the system is then named freezing point of the solvent at the composition and pressure of the system.
- A solid solution of both constituents.

For our purpose, the most interesting point is the second one. This is the reason why we limit our study to it.

From the qualitative standpoint, when a solute is dissolved in a liquid phase, initially pure, the fugacity of the latter is lowered. It becomes weaker than that of the pure solid solvent which was that of the initial pure liquid phase in equilibrium with it. There is a break of the initial liquid–solid equilibrium. In order to recover it, the temperature of the system must decrease. It is the reason why, in this case, the freezing point of the solvent is always lower than the normal freezing point.

13.3.2 Mathematical Expression Linking the Solvent Activity to the Depression of the Freezing Point

In this paragraph, we are seeking for a mathematical expression relating the activity a_1 of the solvent in every solution to the lowering of its freezing point due to the presence of the solute into it. Having this relation in our hands, it is possible to obtain the solvent activity once the freezing point is determined.

In order to set up the relation, one relates the chemical potential μ_s of the solvent in the solid state, at the temperature T, to its activity a_s in the solid pure state through the standard chemical potential $\mu^\circ{}_1$ of the solvent *in the liquid state*. The relation is

$$\mu_s = \mu_1^\circ + RT \ln a_s \tag{13.8}$$

Reasoning in such a manner is unusual but is perfectly legitimate, given the arbitrary character of the definition of an activity. As we shall see it immediately, with this choice, the activity of the pure solvent in the solid state is equal to its activity in solution, the latter varying with the temperature:

$$a_{\mathrm{s}} = a_1$$

It is true that this result may appear to be surprising since with the usually chosen standard states, the activity of a pure compound is constant at given temperature and pressure. This is not the case here as we shall see it. This result apparently paradoxical is due to the fact that the fugacity of the solvent is identical (at constant pressure and for a given temperature in both phases (solid pure and solution)). We have already said that this is a condition of equilibrium (viz. Chap. 7). As a result, since the fugacity of the solvent varies with the temperature and with the composition of the solution, the fugacity of the solid also varies. This is the base of the phenomenon.

Concerning, now, the equality of the activities in both phases, it results from the same reasoning. The activity a_{s} is according to the general definition of an activity:

- For the solid phase (s: solid, l: liquid) $a_{\mathrm{s}} = f_{1(\mathrm{solid})}/f_1{}^{\circ}{}_{(\mathrm{liq})}$
- For the liquid phase $a_1 = f_{1(\mathrm{liq})}/f_1{}^{\circ}{}_{(\mathrm{liq})}$

with $f_{1(\mathrm{solid})} = f_{1(\mathrm{liq})}$ (equilibrium). The fugacity $f_1{}^{\circ}{}_{(\mathrm{liq})}$ is the same in both phases. This is the result of the arbitrary choice of the same standard state. As a result $a_{\mathrm{s}} = a_1$.

13.3.3 Relation Between the Activity of the Solvent and the Temperature of the System

Let us divide the expression (13.8) by T. We obtain

$$R\ \ln a_{\mathrm{s}} = \mu_{\mathrm{s}}/T - \mu_1{}^{\circ}/T$$

Now, let us derivate this expression with respect to T at constant pressure. Given the general expression of the partial derivate with respect to T of the ratio μ/T at constant pressure and composition (viz. Chaps. 2, 5 and 9)

$$[\partial(\mu_i, T)/\partial T]_{p,x} = -\overline{H_i}/T^2$$

we obtain

$$(\partial \ln a_{\mathrm{s}}/\partial T)_{\mathrm{p}} = (H_1{}^{\circ} - H_{\mathrm{s}})/RT^2$$

In this expression, the partial molal enthalpies have disappeared because μ_s and $\mu_l{}^\circ$ are related to the pure solvent in the solid and liquid states. Hence, they are replaced by the molal quantities (viz. Chap. 8, paragraph 8). The enthalpy difference ($H_l{}^\circ - H_s$) is nothing else than the molal fusion heat ΔH_{fusion} of the solvent at the temperature and the pressure of the system:

$$H_l{}^\circ - H_s = \Delta H_{\text{fusion}}$$

in which

$$(\partial \ln a_s/\partial T)_p = \Delta H_{\text{fusion}}/RT^2$$

We have seen that with the chosen standard state, the activity of the pure solvent in the solid state and its activity in solution are equal. As a result

$$(\partial \ln a_1/\partial T)_p = \Delta H_{\text{fusion}}/RT^2 \tag{13.9}$$

This relation gives the change in the activity of the solvent with the temperature at the freezing point at constant pressure. The change varies with the composition. Hence, the expression relating the activity of the solvent at the freezing point can be obtained by integration of this relation.

The integration of (13.9) is performed in the following way. It entails to know the change in ΔH_{fusion} with the temperature. The Kirchhoff's relation (which relates the heat accompanying a chemical or a physical process at a given temperature to that produced by the same process at another temperature) is written in the present case, since the heat of fusion ΔH_{fusion} is referred at constant pressure:

$$\begin{aligned}[\partial(\Delta H_{\text{fusion}})/\partial T]_P &= (C_P)_l - (C_P)_s\\ [\partial(\Delta H_{\text{fusion}})/\partial T]_P &= \Delta C_P\end{aligned} \tag{13.10}$$

$(C_P)_l$ and $(C_P)_s$ are the molar calorific capacities at constant pressure of the solvent in the pure liquid state and in the pure solid state. One can admit that, for a break change in temperature, the calorific capacities are constant. Then, the integration of equation (13.10) gives

$$\Delta H_{\text{fusion}} + L_0 + \Delta C_P(T\text{-}T_0) \tag{13.11}$$

L_o is the integration constant. It is the molar latent heat of fusion at temperature T_0, freezing temperature of the pure solvent.

It is simpler, for the sake of simplification of the calculations, to change the variable in order to continue the mathematical development. We adopt the variable θ such as

$$T_0 - T = \theta$$

θ is the depression of the freezing point. Equation (13.11) becomes

$$\Delta H_{\text{fusion}} = L_0 - \theta \Delta C_P \tag{13.12}$$

The expression which must be integrated is

$$d \ln a_1 = \left[(L_0 - \theta \Delta C_P)/RT^2\right] dT$$

Since $dT = -d\theta$ and $T = T_0 - \theta$, it becomes

$$-d \ln a_1 = \left[(L_0 - \theta \Delta C_P)/R(T_0 - \theta)^2\right] d\theta \tag{13.13}$$

The integration can be performed by developing the term $1/(T_0 - \theta)^2$ according to Newton's binomial. This term can also be written as $1/{T_0}^2(1 - \theta/T_0)^{-2}$, in which

$$1/(T_0 - \theta)^2 = 1/T_0^2\left(1 + 2\theta/T_0 + 3\theta^2/T_0^2 + \cdots\right)$$

Equation (13.13) becomes

$$-d \ln a_1 = 1/RT_0^2[L_0 + (2L_0/T_0 - \Delta Cp)\theta +] d\theta \tag{13.14}$$

The integration is performed in the domain of the values of θ going from 0 until the value of θ, respectively, corresponding to the limits $a_1 = 1$ and a_1. The integration is immediate and gives, after having neglected the terms in θ^3, θ^4, ... since the weak value of θ:

$$-\ln a_1 = L_0\theta/RT_0^2 + \theta^2/RT_0^2(L_0/T_0 - \Delta Cp/2) \tag{13.15}$$

The expression (13.15 permits to determine the activity of the solvent a_1 knowing the depression of the freezing point.

Let us recall that the relation (13.15 gives the activity of the solvent at temperatures which vary with the solute concentration of the solution. It is desirable to transform the results obtained in this way into results at the same temperature. This point is studied in Chap. 14.

Broadly speaking, the depression of the freezing point θ is of the order of the 1/10 °C for solutions, the concentrations in solutes of which are lower than 0.5 mol kg $^{-1}$. (Let us notice that it is relatively easy to measure differences of temperature of the order of 10^{-4} °C between an aqueous solution in equilibrium with ice and pure water.)

13.4 Activity of the Solvent and Osmotic Pressure

In principle, the measurement of the osmotic pressure permits the determination of the activity a_1 of the solvent of a binary solution. It is based on the existence of a relation between the solvent activity and the osmotic pressure.

One knows (viz. Chap. 8) that, in order to recover the initial equilibrium, after the system has given rise to the phenomenon of osmosis, one must apply a supplementary pressure $\pi = P - P_0$, called osmotic pressure, to the solution constituting the system. P is the pressure above the solution before the initial equilibrium has been recovered. P_0 is the pressure above the compartment containing the pure solvent. (Let us recall that the osmotic pressure must be applied at constant temperature and number n_2 of moles of the solute.) Let μ_{01} and μ_1 be the chemical potentials of the pure solvent and of the solution before the initial equilibrium (broken by the addition of the solute) is recovered. After it is the case, the following equality is satisfied:

$$\mu_{01} = \mu_1 + \int_{p_0}^{P} (\partial\mu_1/\partial P)_{T,n2}dp$$

The partial derivative $(\partial\mu_1/\partial P)_{T,n2}$ is equal to the partial molal volume of the solvent in the solution (viz. Chap. 5):

$$(\partial\mu_1/\partial P)_{T,n2} = \overline{V_1}$$

Thus

$$\mu_{01} = \mu_1 + \int_{p_0}^{p} \overline{V_1}dp \tag{13.16}$$

The chemical potentials are related to the fugacities in the pure state $f_1{}^\circ$ and in the solution f_1 at the pressure P_0 by the relations (viz. Chap. 9)

$$\mu_{01} = \mu_1^* + RT\ \ln f_1{}^\circ \quad \text{and} \quad \mu_1 = \mu_1^* + RT\ \ln f_1$$

After substitution into (13.16), we obtain

$$RT\ \ln(f_1{}^\square/f_1) = \int_{p_0}^{p} \overline{V_1}\,dP \tag{13.17}$$

By definition, the inverse of the above ratio of the fugacities is the activity a_1 of the solvent:

$$a_1 = f_1/f_1^{\square}$$

in which

$$-RT \ln a_1 = \int_{p_0}^{p} \overline{V_1}\, dP$$

In order to set up the relation between the activity of the solvent and the osmotic pressure, it remains, evidently, to know the changes of $\overline{V_1}$ with the external pressure. Assuming that they are linear, one can write at every pressure

$$\overline{V_1} = \overline{V_0}\,[1 - \alpha(P - P_0)]$$

where $\overline{V_0}$ is the partial molal volume at the pressure p_0 (1 atm) and α is a constant. Introducing this hypothesis, we obtain

$$-RT \ln a_1 = \overline{V_0}\int_{p_0}^{p} [1 - \alpha(P - P_0)]dP$$

$$-RT \ln a_1 = \overline{V_0}(P - P_0)[1 - (1/2)\alpha(P - P_0)]dP$$

and finally

$$-RT \ln a_1 = \overline{V_0}\,\pi[1 - (1/2)\alpha\pi] \qquad (13.18)$$

This is the relation being searched for. In several cases, the partial molal volume $\overline{V_0}$ at pressure P_0 is purely and simply replaced by the molal volume V_0 of the pure solvent in the preceding relation.

In practical use, the process consisting in determining the activity a_1 through the measurement of π is not satisfactory. One of the difficulties it encounters is that it is difficult to have a true semipermeable membrane at our disposal. Another difficulty lies in the knowledge of the change in the partial molal of the solvent with the pressure and the concentration. This is the reason why using the process based on the osmotic coefficients is preferred. Its study is deferred to Chap. 14 since it is overall used to determine the mean ionic activity coefficients.

13.5 Determination of the Activities of Nonelectrolytes by Measurements of the Electromotive Forces

13.5.1 General Considerations

Let us recall that the determination of the activities of nonelectrolytes (and of electrolytes) is possible through the measurements of electromotive forces (emf) of judiciously designed electrochemical cells (viz. Chap. 5). The emf of a cell may depend on the activities of the species participating in the reactions occurring onto the electrodes or on the activities of the species chemically reacting with the preceding ones (viz. Chap. 14). In some galvanic cells, the emf may also depend on the composition of the electrolyte in the cell. Finally, there still exist cells in which the emf only depends on the state of the electrode. It is the case of some concentrations of galvanic cells without a liquid junction (viz. Chap. 14). It is the case of the galvanic cells equipped with electrodes constituted by metallic solutions of changing concentrations such as metallic alloys or amalgams of different compositions. This kind of cell is represented, for example, by

$$\mathrm{Me(Hg)}, x_2' \big| \mathrm{Me\,X} \big| \mathrm{Me(Hg)},\, x_2$$

Both electrodes are amalgams of different concentrations x_2' and x_2 in the metal Me. In these caculations, they dip into the same solution of the electrolyte MeX. The experience shows that an emf creates, the value of which does not depend on the concentration of the electrolyte but depends on the activities of the metal in the amalgams, whence the used process.

13.5.2 Example of the Determination of the Activity of Thallium in an Amalgam

An example of the previous process is provided by the use of the cell, the electrodes of which are constituted by two thallium amalgams of different concentrations. The measurements of the emf in some conditions permit to obtain the activities of thallium (and even of the mercury—viz. above and later in this chapter) in both metallic solutions constituting the electrodes.

Let us consider a galvanic cell, the electrodes of which are thallium amalgams of different molar fractions, x_2 and x_2'. The electrolyte is an aqueous solution of a thallous salt. The cell is represented by the following scheme:

$$\mathrm{Tl}\left(\text{amalgam } x_2'\right)\big|\text{thallous salt}\big|\mathrm{Tl}\left(\text{amalgam } x_2\right)$$

Both electrochemical reactions are as follows:

- For the electrode on the left (in the occurrence the electrode playing the part of the anode since we are faced with a pile):

$$\mathrm{Tl} \rightleftharpoons \mathrm{Tl}^+ + 1\mathrm{e}^-$$

– For the cathode:

$$\mathrm{Tl^+ + 1e^- \rightleftharpoons Tl}$$

There is no global reaction of cell. The sole net process occurring is the transformation

$$\mathrm{Tl}\left(\text{amalgame}, x_2'\right) \rightarrow \mathrm{Tl}(\text{amalgame},\ x_2)$$

The difference in Gibbs energy ΔG accompanying the transfer of one mole of thallium from the anode to the cathode is equal to the difference of the chemical potentials μ_2 and μ_2' of thallium in both amalgams, that is to say,

$$\begin{aligned} \Delta G &= \mu_2 - \mu_2' \\ \Delta G &= RT\ \ln\left(a_2/a_2'\right) \end{aligned} \tag{13.19}$$

The crossing of one mole of thallium from one electrode to the other involves the crossing of one faraday of electricity. The "increase" of the Gibbs energy of the system ΔG accompanying the transfer is given by the expression

$$\Delta G = -1FE \tag{13.20}$$

F is the faraday ($1\,F = 96{,}485\ \mathrm{C\ mol^{-1}}$) and E the observed potential difference in the conditions of the determination. 1 is the number of electrons exchanged between the two redox couples intervening in the global (virtual) reaction (of cell). The measurement of E (at null current—viz. Chap. 5) permits to obtain the ratio of activities. The comparison of the expressions (13.19) and (13.20) shows that

$$E = -(RT/F)\ln\left(a_2/a_2'\right) \tag{13.21}$$

13.5.3 *Determination of the Activity of the Metal in the Amalgam*

Actually, the measurement of E also permits to reach the activity of the metal in the amalgam and not only the ratio of both activities, but this is solely possible after the standard state of the metal has been fixed.

For the sake of illustration of the whole previous considerations, the activity of the metal is determined after having chosen two different standard states.

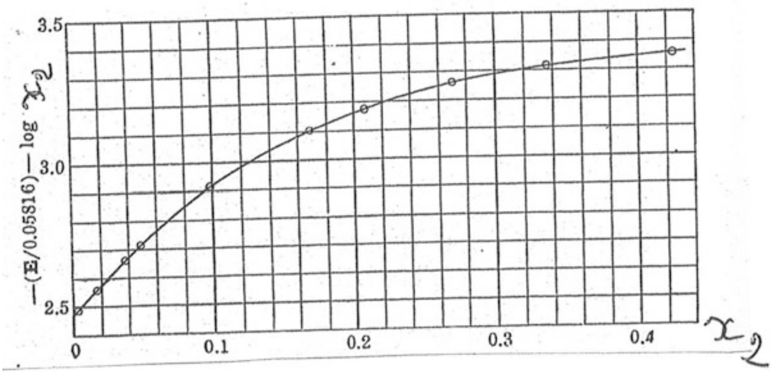

Fig. 13.5 Determination of the activity of thallium in the amalgams at 20 °C and $x_2^{'} = 0.00326$ *(According to G.N. Lewis and M. Randall: Thermodynamics and the free energy of chemical substances: McGraw-Hill company, Inc, New York, 1923)*

- Let us choose the standard state in such a way that the activity coefficient a_2/x_2 is equal to 1 at infinite dilution.

  Equation (13.21) can be equivalently written as

$$\ln a_2 = -EF/RT + \ln a_2'$$

Let us subtract $\ln x_2$ from the two members of the equality. We obtain

$$\log(a_2/x_2) = (-EF/2.303RT - \log x_2) + \log a_2' \qquad (13.22)$$

In order to apply this relation, one builds a series of cells in which the composition x_2 of the electrode on the right varies, whereas the concentration $x_2^{'}$ of the electrode on the left is constant. The emf E of the different cells is measured and the different values of the term in the brackets in relation (13.22) are brought on a diagram as a function of the concentration x_2. The curve is shown in Fig. 13.5.

When $x_2 = 0$ (infinite dilution), according to the choice of the standard state, $a_2/x_2 = 1$ $\log(a_2/x_2) = 0$. (*It is at this point that we can recognize that we adopt this standard state*.) The value of the term in brackets is then equal to $-\log a_2^{'}$. It is at the value (2.4689) that the previous curve cuts the ordinates axis. Its corresponds to the value $a_2^{'} = 0.003396$. Then, one can determine the ratio a_2/x_2 and hence a_2 in each of the amalgams by applying (13.21). The different obtained values are mentioned in Table 13.2.

We notice that as soon as the amalgams are no longer sufficiently dilute, the activities considerably move away from the concentrations x_2 as it is indicated by the values $a_2/x_2 = \gamma_2$. It is understood that the deflection with respect to unity of the coefficient γ_2 quantifies the deviation of the system with respect to Henry' law, given the standard state.

- Let us now choose the pure liquid thallium at 20 °C. In that case, the electrochemical used is symbolized by

$$\mathrm{Tl}\left(\text{pure liquid}, x_2' = 1\right)\left|\text{Thallous salt}\right|\mathrm{Tl}\,(\text{amalgam}\,, x_2)$$

Let us notice that the standard state is already chosen by setting up $x_2' = 1$ in the electrode on the left. Now, the relation (13.21) is

$$E = -(RT/F)\ln(a_2/1) \tag{13.23}$$

The thallium activity in the amalgam can be directly calculated from measurements of E. However, there is a difficulty; thallium melts at 302 °C and the cell symbolized above cannot exist. The difficulty can be overcome as follows. The process consists in extrapolating the values a_2/x_2 as a function of x_2 (viz. Table 13.3) until $x_2 = 1$ which defines a new standard state, differing from the previous one. Given the fact that all the values used for the extrapolation are obtained by working with liquid amalgams at 20 °C, the obtained value 8.3 corresponds to the pure thallium in supercooling. Since $a_2/x_2 = 8.3$, in the standard state and since $x_2 = 1$, the result is that the activity of thallium is $a_2 = 8.3$. But, given the fact that the values a_2/x_2 used above to perform the extrapolation have been established starting from the previous standard state based on Henry's law, the value $a_2 = 8.3$ is that of pure thallium in supercooling *based on the standard state defined in such a way that at infinite dilution the activity is equal to its molar fraction.*

However, adopting a standard state entails the fact that the activity of the species must be equal to unity in it. To sum up, we can write:

a_2 (pure supercooled thallium, 20 °C) = 8.3 (standard state: infinite dilution, 20 °C)

a_2 (pure supercooled thallium, 20 °C) = 1 (standard state: pure supercooled thallium 20 °C)

Let us recall that the ratio of the activities of the same species (in the same thermodynamic state), based on two different standard states, is constant. Once more, these results constitute an illustration of the fact that the activity of a substance, in a given thermodynamic state, exhibits different numerical values according to the choice of the standard state. As a result, the values of the constants of equilibria involving these substances present different numerical values (viz. Chap. 17). In continuation of the previous reasoning, the values of the activities a_2 in the different amalgams of Table 13.3, based on the standard state at infinite dilution, must be, of course, systematically divided by the factor 8.3 in order to obtain their values in the new standard state.

The method, just described above, has been used in order to determine the activity of a metal in another one, that is to say, in a liquid alloy or in other

Table 13.3 Activity of thallium in some amalgams at 20 °C

x_2	$-E$	$\frac{-E}{0.05816} - \log x_2$	$\frac{a_2}{N_2}$	a_2
0	$-\infty$	2.4689	1	0
0.003259	0	2.4869	1.042	0.003396
0.01675	0.04555	2.5592	1.231	0.02062
0.03723	0.07194	2.6660	1.574	0.05860
0.04850	0.08170	2.7184	1.776	0.08624
0.0986	0.11118	2.9177	2.811	0.2772
0.1680	0.13552	3.1045	4.321	0.7259
0.2074	0.14510	3.1780	5.118	1.061
0.2701	0.15667	3.2610	6.196	1.674
0.3361	0.16535	3.3159	7.031	2.363
0.4240	0.17352	3.3558	7.707	3.268
0.428 (sat.)[1]	0.17387	3.3580	7.75	3.316
Tl (liquid, supercooled)			8.3	8.3

amalgams. Let us mention the determination of lead in an alloy of lead and bismuth, of bismuth or cadmium or potassium in amalgams.

13.5.4 *Activity of the Mercury*

As it has been said above, the previous process also permits to determine the activity of the other component of a binary mixture. In the case of amalgams such as that of thallium, the values of the activities of thallium, obtained as described, permit to reach those of mercury by using the Gibbs–Duhem's relation (viz. the beginning of this chapter).

13.6 Determination of the Activities of Nonelectrolytes with Varied Instrumental Methods

Here, we confine ourselves to the description of a method based on the use of the chromatography in vapor phase. It is named "inert gas stripping and gas chromatography." It consists in determining the decrease of the concentration of the solute (the activity of which being asked for) in the gaseous phase as a function of time as its elimination from the liquid phase is in progress because of the bubbling of the inert gas into it. The concentration in the vapor phase is of course determined by gas chromatography.

The activity coefficients determined in such a manner are those at infinite dilution. The method exhibits the advantage to be a kinetic one. The values are extracted from the decreasing curve. Hence, we can cast off the value of the initial concentration which is at least quite uncertain, given the high dilutions used.

13.7 Determination of Activities Through Excess Functions and Calculation of Activities Through Empirical Relations

Thermodynamic properties of solutions, in particular those of mixtures of nonelectrolytes, are frequently studied through consideration of excess functions. They are quantities by which the Gibbs energy, entropy, and other thermodynamic functions differ from the corresponding ones of an ideal solution of same composition. In particular, the excess Gibbs energy is related quasi-directly to the activity coefficients, where there is the existence of another process of determination of activities. Otherwise, we know that there exist empirical relations of the type of those of Margules and van Laar (viz. Chap. 8). They permit to fairly well calculate the fugacities and hence the activities of the components of nonideal solutions.

Let us slightly anticipate what is described in Chap. 16. Of utmost importance is the notion of excess Gibbs energy G^{E} which is experimentally accessible. It permits to determine the activity coefficients. One of the methodologies consists in finding mathematical relations between this quantity and the molality m (or the molar fraction x) of the solutes. This is done by starting from experimental data. Most of the time, these relations are polynomial.

For example, in the case of only one nonelectrolyte solute, the following relation is satisfactory:

$$\left(G^{\mathrm{E}}/w_{\mathrm{s}}RT\right) = \lambda m^2 + \mu m^3 + \cdots$$

w_{s} is the mass of the solvent and λ and μ are fitting parameters. We shall see that, after derivation, one can obtain the activity coefficient of the solute γ and the practical osmotic coefficient ϕ_{m} (viz. Chap. 14) according to the relations

$$\ln\gamma = 2\lambda m + 3\mu m^2 + \cdots$$
$$\phi_{\mathrm{m}} - 1 = \lambda m + 2\mu m^2 + \cdots$$

λ and μ must be, of course, known. This is realized by fitting the experimental data of G^{E} to the molalities or molar fractions.

We defer the study of these means of calculation of activities to Chap. 16.

Table 13.4 Activities of saccharose and water in aqueous solutions as a function of the molality of saccharose (*According to R.A. Robinson, R.H. Stokes, Electrolyte Solutions,* 2nd *Ed, Dover Publications Inc, 2002, New York)*

M	a_w	ϕ	$\log \gamma$
0.1	0.99819	1.0072	0.0062
0.3	0.99449	1.0226	0.0193
0.5	0.99068	1.0393	0.0333
0.7	0.98676	1.0569	0.0479
0.9	0.98272	1.0754	0.0631
1.2	0.97641	1.1044	0.0868
1.6	0.96755	1.1447	0.1197
2.0	0.95818	1.1857	0.1535
3.0	0.93284	1.2863	0.2382
4.0	0.90560	1.3761	0.3185
5.0	0.8776	1.4500	0.3906
6.0	0.8496	1.5084	0.4541

13.8 Some Results

At concentrations lower than 0.1 mol kg^{-1}, the difference between the activity of a non-charged species does not differ from its concentration by a deflection larger than 1 p 100. This is the reason why in dilute solutions, the activity coefficients are taken to be equal to unity during, for example, the calculations involving chemical equilibria. In Table 13.4, we give the activities of water and saccharose as a function of the molality of the latter. The activity coefficients of uncharged molecules are generally higher than unity.