

Related topics

Raoult's law, cryoscopic constants, chemical potential, Gibbs-Helmholtz equation, concentration ratio, degree of dissociation, Van't Hoff factor, cryoscopy.

Principle and task

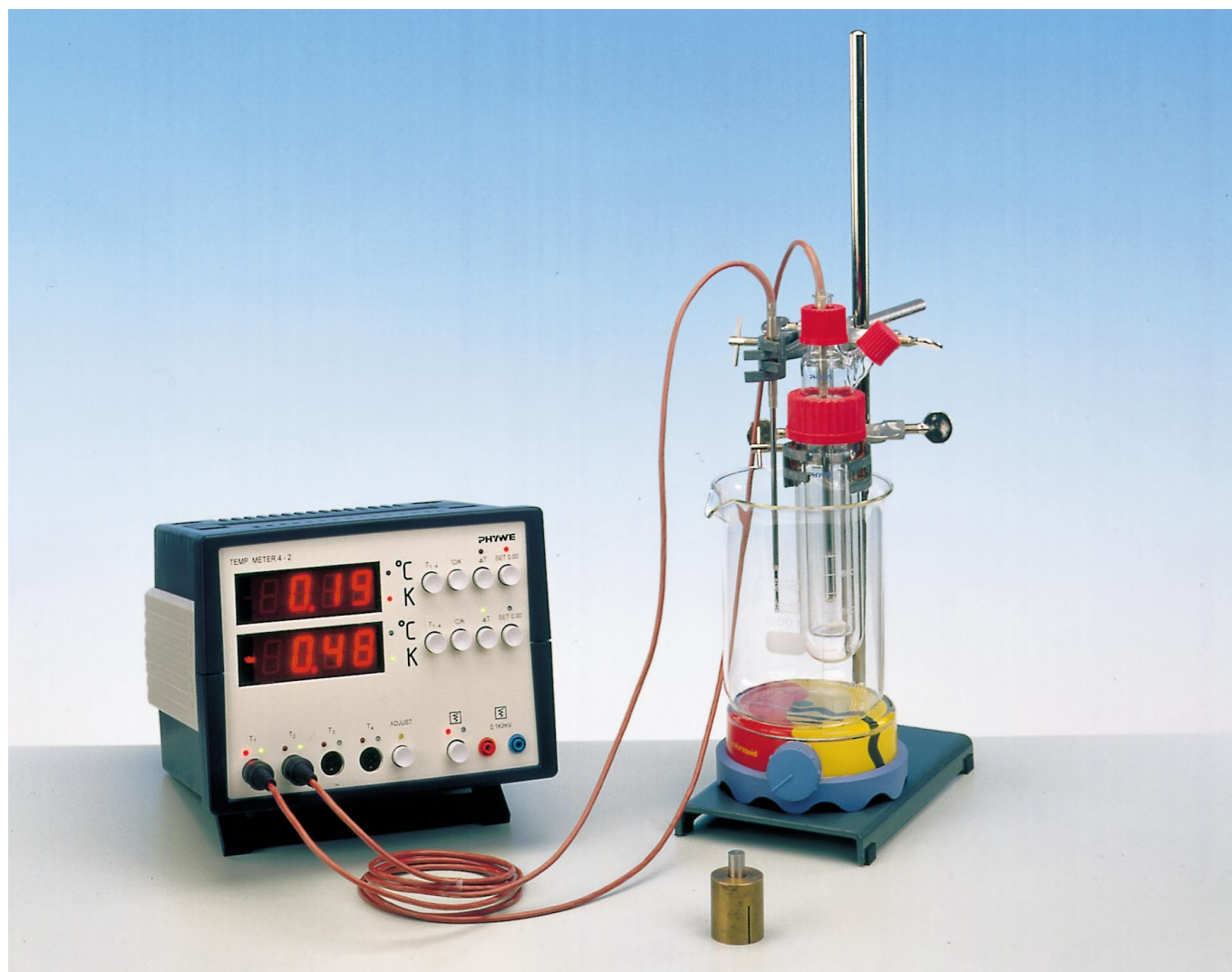
The freezing point of a solution is lower than that of the pure solvent. The depression of the freezing point can be determined experimentally using a suitable apparatus (cryoscopy). If the cryoscopic constants of the solvent are known, the molecular mass of the dissolved substances can be determined.

Equipment

App. for freezing point depr.	36821.00	1
Jointing f. GL25, 12 mm hole, 10 pcs	41243.03	1
Temperature meter digital, 4-2	13617.93	1
Temperature probe, immers. type	11759.01	2
Protective sleeves f. temp.probe, 2	11762.05	1
Pellet press for calorimeter	04403.04	1

Magn. stirrer, mini, controlable	35712.93	1
Right angle clamp	37697.00	2
Universal clamp	37715.00	2
Glass beaker, short, 1000 ml	36017.00	1
Volumetric pipette, 50 ml	36581.00	1
Pipettor	36592.00	1
Retort stand, h 1000 mm	37695.00	1
Wash bottle, plastic, 500 ml	33931.00	1
Magn.stirring bar 15 mm, cyl.	46299.01	1
Balance SBA42, 120 g/1 mg, ext. Cal.	46034.93	1
Stopwatch, digital, 1/100 sec.	03071.01	1
Mortar w. pestle, 70 ml, porcelain	32603.00	2
Microspoon, special steel	33393.00	1
Spoon, special steel	33398.00	1
Funnel, plastic, dia. 50 mm	36890.00	1
Weighing dishes, 85×85× 7 mm, 100	45019.01	1
Pasteur pipettes, 250 pcs	36590.00	1
Rubber caps, 10 pcs	39275.03	1
Glass rod, boro 3.3, l = 300 mm, d = 8 mm	40485.06	1
Sodium chloride 500 g	30155.50	1
Hydroquinone 250 g	30089.25	1
Raw alcohol for burning 1000 ml	31150.70	1

Fig. 1: Experimental set-up: Freezing point depression.



Problems

1. Determine the size of freezing point depression after dissolving a strong electrolyte (NaCl) in water. By comparing the experimental value with the theoretical one predicted for this concentration, determine the number of ions into which the electrolyte dissociates.
2. Determine the apparent molar mass of a non-electrolyte (hydroquinone) from the value of freezing point depression.

Set-up and procedure

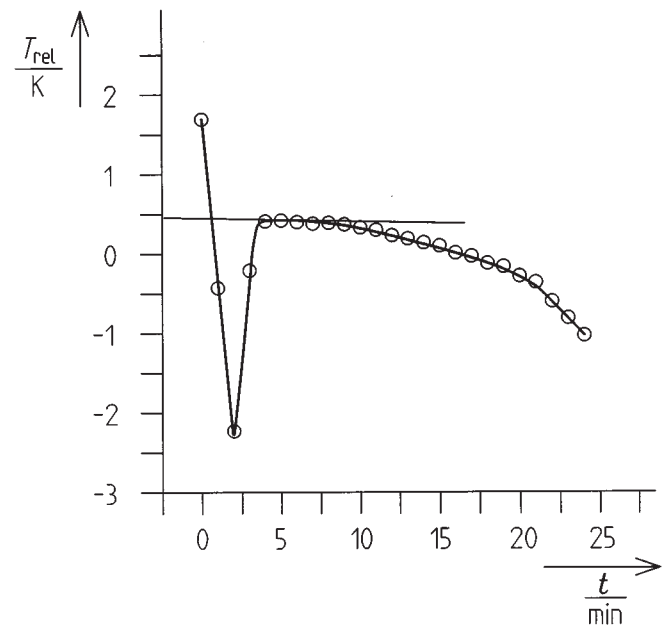
Perform the experimental set-up shown in Figure 1. The apparatus for depression of the freezing point consists of two cylindrical glass vessels, arranged concentrically and connected with a GL 45 screw assembly. The outer vessel, similar in shape to a test tube, forms a jacket around the inner vessel (freezing vessel). The jacket is filled with approximately 35 to 40 ml of ethanol (raw alcohol can also be used). This intermediating medium (ethanol) ensures that heat conductance between the inner and outer vessels is uniform. The inner vessel is intended for the solution or the solvent whose freezing point is to be determined. On the upper end of the inner vessel there is a screw cap for a thermometer or a temperature probe and a tubular glass sleeve with a screw cap (GL 18) for introducing the substance which is to be dissolved. The base of the inner vessel is flat so that a small stirring bar ($l = 15$ mm) can rotate without hindrance.

Press the substances to be investigated into pellets to prevent any particles of the substance from sticking to the walls of the vessel during introduction. Measure each of the substances (NaCl, hydroquinone) into approximately 600 mg portions. It is advisable to pulverise the substances with a mortar and pestle. To operate the pellet press, proceed as follows: first insert the small steel cylinder and then place the press in upright position. Using a funnel, fill the weighed substance into the pellet press, insert the large plunger and apply medium pressure using the vice to press the pellet. Then deburr the pellets, and weigh them (weighing accuracy 1 mg).

The measurement consists of two steps. First, the cooling curve of the pure water is plotted, followed by that of the solution (after the substance has been added).

In order to perform the test exactly, pipette 50 ml distilled water with the volumetric pipette into the inner vessel, and carefully add a magnetic stirrer bar ($l = 15$ mm). Now insert the protective sleeve for the temperature sensor into the screw connection, whereby the seal of the screw connection is replaced with the seal having a bore which is 12 mm in diameter. Now, drop two or three drops of raw alcohol onto the protective sleeve to ensure improved heat transfer, and insert the immersion type temperature probe. Then connect the probe to the digital temperature meter. When the apparatus is fully assembled, fix the device to the support rod and position it as low as possible in the 1000 ml beaker (Fig. 1). Set the magnetic stirrer to medium stirring speed. First set the display on the digital temperature meter for the probe in the inner vessel of the apparatus to the degrees Celsius ($^{\circ}\text{C}$) mode, and then fill the beaker with the ice/salt mixture. Now immerse a second immersion type temperature probe PT 100 in the ice mixture (control). The temperature of the freezing mixture should be set to around -10°C by adding water. When the temperature has reached approximately -1°C , set the digital temperature

Fig. 2. Cooling curve of water/table salt (NaCl) mixture.



meter to measure the change in temperature overtime ΔT for the temperature probe in the inner vessel in accordance with the instruction manual (accuracy of temperature measurement 0.01 K). Now, record the relative temperatures which are displayed.

In the initial phase a metastable condition, which is characterised by a temperature minimum, develops. As soon as crystallisation starts, the temperature begins to rise again and reaches the arrest level, which, depending on the mixture, either has an obvious kink or gradually changes into a sinking cooling curve. The cooling curve must be measured for a sufficient period of time in order to be able to extrapolate it (compare Fig. 2.). The intersection point with the initial part of the curve is the critical point; it is entered as the freezing point in the evaluation.

After the cooling curve of 50 ml of pure water has been recorded in this manner, lift the apparatus out of the freezing mixture and wait until the water in the inner vessel has completely liquefied again. This process can be speeded up by hand warming. Do not change the ΔT setting on the digital temperature meter. When the water has completely reliquefied, introduce a pellet of the substance under investigation into the inner vessel through the lateral connecting sleeve, and wait until the substance has dissolved completely. Then relower the apparatus into the freezing mixture. When the relative temperature reaches the initial value of the first test measurement, record the temperature again every minute. The resulting plot allows the freezing point of the mixture to be determined, again using extrapolation (Fig. 2). Thoroughly clean and dry the inner vessel before each new measurement is performed.

Theory and evaluation

If a small amount of a substance B is dissolved in a pure solvent A, the fusion temperature of the solution falls below that of the pure solvent A. However, the precondition for this is that pure solvent crystallises out, i.e. A and B should not form mixed crystals. The chemical potential μ_A^l of substance A in the mixed phase at a high concentration of A is

$$\mu_A^l = \mu_A^{\circ l} + RT \ln x_A \quad (1)$$

The chemical potential of the pure solid phase μ_A^s in equilibrium with the fluid phase corresponds to the chemical standard potential $\mu_A^{\circ s}$ of A, i.e. $\mu_A^s = \mu_A^{\circ s}$. When both phases are in equilibrium $\mu_A^s = \mu_A^l$ and the following expression is obtained:

$$\mu_A^{\circ l} = \mu_A^{\circ s} + RT \ln x_A \quad (2)$$

Since the chemical potential of pure substances is identical with the molar free enthalpy G° , equation (2) becomes

$$G_A^{\circ l} - G_A^{\circ s} = RT \ln x_A \quad (3)$$

From the Gibbs-Helmholtz equation

$$\frac{d(G/T)}{dT} = -\frac{H}{T^2}; p = \text{const.} \quad (4)$$

and through differentiation of equation (3), the following is obtained

$$\frac{H_A^{\circ s} - H_A^{\circ l}}{RT^2} = \frac{\Delta_F H}{RT^2} = \frac{d \ln x_A}{dT} \quad (5)$$

The fusion enthalpy $\Delta_F H$ can be considered as constant for small temperature changes. Integration of (5) between the limiting values for the pure solvent ($x_A = 1, T = T_0$) and for solution (x_A, T) results in the expression

$$-\ln x_A = \frac{\Delta_F H}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) = \frac{\Delta_F H}{R} \left(\frac{T - T_0}{TT_0} \right) \quad (6)$$

Because the freezing point depression $\Delta T_F = T - T_0$ is small in comparison with T_0 the term TT_0 can be replaced with T_0^2 . If the amount x_B of the solute is considered concurrently, then x_A can be replaced with $1 - x_B$. This results in

$$\frac{\Delta_F H}{R} \left(\frac{T - T_0}{T_0^2} \right) = -\ln(1 - x_B) \quad (7)$$

Equation (7) can be developed as a series:

$$\frac{\Delta_F H}{RT_0^2} \cdot \Delta T_F = x_B + \frac{1}{2}x_B^2 + \frac{1}{3}x_B^3 \dots \quad (8)$$

Where x_B is small, only the first linear term need be considered. The freezing point depression then reduces to

$$\Delta T_F = \frac{RT_0^2}{\Delta_F H} \cdot x_B \quad (9)$$

In dilute solutions the amount of substance can be expressed as a good approximation by the quotients $(m_B M_A / m_A M_B)$. M_A , M_B and m_A , m_B are the molar masses and the weighed masses of solvent A and solute B, respectively.

$$\Delta T_F = \frac{RT_0^2}{\Delta_F H} \cdot \frac{m_B M_A}{m_A M_B} = \frac{RT_0^2}{\Delta_F H} M_A \cdot \frac{m_B}{m_A M_B} \quad (10)$$

Finally, the fraction $m_B / m_A M_B$ is equal to $m/1000$, in which m represents the molality, i.e. the amount of solute in 1000 g of solvent.

$$\Delta T_F = \frac{RT_0^2}{\Delta_F H} M_A \cdot \frac{m}{1000} = K_K \cdot m \quad (11)$$

The constant K_K is known as the molar freezing point depression or the cryoscopic constant.

When determining the molar mass of a dissolved substance, the fact that the number of free moles N_B corresponds with the number of freely moving particles must be taken into consideration. However, if n_B moles dissociate into z smaller particles in solution, then the number of actually existing moles is

$$n = n_B (1 + (z - 1)\alpha) \quad (12)$$

where α is the degree of dissociation.

Under certain conditions, the determination of the molar mass with cryoscopy may therefore only provide the apparent molar mass M_s which has then to be converted using

$$M_s = \frac{M_B}{1 + (z - 1)\alpha} \quad (13)$$

Where concentrations are higher, the interionic interactions of the existing ions has also to be taken into consideration. The osmotic coefficient f_0 is used to describe this interaction. It has a value between 0 and 1 for real solutions and a value of 1 for ideal solutions.

$$n = n_B (1 + (zf_0 - 1)\alpha) \quad (12)$$

The effective amount of substance in the solution differs from the value used by an amount equal to the Van't Hoff Factor $i = (1 + (zf_0 - 1)\alpha)$. It therefore follows analogously that the experimental freezing point depression is greater than the theoretical value calculated from the weighed amounts by a factor i .

Data and results

$$K_K (\text{water}) = 1.86 \text{ k} \cdot \text{kg} \cdot \text{mol}^{-1}$$

The apparent molar mass of table salt was experimentally determined to be $29.58 \text{ g} \cdot \text{mol}^{-1}$. The literature value is $58.443 \text{ g} \cdot \text{mol}^{-1}$. Consequently, for $\alpha = 1$ and $f_0 = 1$ a dissociation ratio of 1:2 results.

Molar mass of hydroquinone (in $\text{g} \cdot \text{mol}^{-1}$; $\alpha = 0$):
106.87 (Exp.); 110.11 (Lit..)