

## Related topics

Raoult's law, Henry's law, ebullioscopic constants, chemical potential, Gibbs-Helmholtz equation, concentration ratio, degree of dissociation.

## Principle and task

The boiling point of a solution is always higher than that of the pure solvent. The dependence of the temperature difference (elevated boiling point) on the concentration of the solute can be determined using a suitable apparatus.

## Equipment

Appar. for elev. of boiling point	36820.00	1
Heat. mantle f. round bott.fl. 250 ml	47550.93	1
Clamp for heating mantle	47557.01	1
Power regulator	32247.93	1
Laboratory balance, data outp. 620 g	45023.93	1
Weighing dishes, 85×85×7 mm, 100	45019.01	1
Temperature meter, digital, 4-2	13617.93	1
Temperature probe, immers.type	11759.01	1
Protective sleeves f. temp. probe, 2	11762.05	1
Retort stand, h 750 mm	37694.00	1
Right angle clamp	37697.00	3

Universal clamp		37715.00	3
Flask, round, 1-neck, 250 ml, GL25/13		35812.15	1
Glass beaker, tall, 250 ml		36004.00	1
Jointing f. GL25, 8 mm hole, 10 pcs		41242.03	1
Silicone tubing i.d. 7 mm		39296.00	1
Mortar w. pestle, 150 ml, porcelain		32604.00	3
Pinchcock, width 15 mm		43631.15	1
Microspoon, special steel		33393.00	1
Wash bottle, plastic, 500 ml		33931.00	1
Pellet press for calorimeter		04403.04	1
Funnel, glass, top dia. 80 mm		34459.00	1
Pasteur pipettes, 250 pcs		36590.00	1
Rubber caps, 10 pcs		39275.03	1
Beads, 200 g		36937.20	1
Sodium chloride	500 g	30155.50	1
Urea	250 g	30086.25	1
Hydroquinone	250 g	30089.25	1
Glycerol	250 ml	30084.25	1
Water, distilled	5 l	31246.81	1

## Problems

1. Measure the increase in boiling point of water as a function of the concentration of table salt, urea and hydroquinone.
2. Investigate the relationship between the increase in boiling point and the number of particles.
3. Determine the molar mass of the solute from the relationship between the increase in boiling point and the concentration.

Fig. 1: Experimental set-up: Boiling point elevation.



## Set-up and procedure

Perform the experimental set-up as described in Fig. 1. Push the protective sleeve for the temperature probe, to which two drops of glycerine are added to improve heat conduction, into the GL screw top of the inner vessel of the boiling point apparatus. In this way the apparatus can be operated with the temperature immersion probe PT 100 and the digital temperature meter 4-2. Having prepared the dry, clean inner vessel in this way, weigh it and record its mass. During the measurement, steam enters the inner vessel through the lateral aperture. When assembling, pay particular attention to ensure that this opening is not covered and is located below the silicone rubber seal of the connecting cap. Slip two short pieces of silicone tubing onto the two gas outlets of the outer vessel and place the free ends in the 250 ml glass beaker. The escaping water vapour can condense here. Attach a hose clip to the lower of the two tubes coming from the outer vessel, and which is initially left open. The round flask is filled with 150 to 200 ml of water, into which a number of beads are placed.

Press the substances to be tested into pellets in order to prevent any particles of the substance from sticking to the walls of the vessel while being added. Five portions of each substance (NaCl, urea, hydroquinone) are weighed out: each should weigh approximately 700 mg. It is advisable to first pulverise the substances with a mortar and pestle. First insert the small steel cylinder into the pellet press, and place the press in a vertical position. Now pour the weighed substance into the pellet press through a funnel. Next fit the large plunger; form a pellet in a vice by applying medium pressure. Deburr the pellets and then weigh them (weighing accuracy 1 mg).

The dependence of the boiling point elevation of water on the concentration can be demonstrated for each substance in one experiment by successively adding known amounts of the same substance. First, weigh the dry inner vessel exactly, and then add 40 ml water; assemble the apparatus and heat it up. The heating rate is controlled with the power control. The temperature in the inner vessel is displayed on the digital temperature meter in degrees Celsius. When the boiling point is reached, lower the heating hood for a short time until boiling stops. In this way the condensate on the outer vessel returns to the round flask. Then raise the heating hood again. When boiling recommences, close the pinchcock. The (slightly superheated) steam now flows through the water in the inner vessel. Set the digital temperature meter to measure the change in temperature  $\Delta T$  over time in accordance with instruction manual (accuracy of temperature measurement 0.01 K) and wait until the value displayed remains constant. By depressing the  $\Delta T$  button again, the relative boiling temperature can be reset to 0 K and the device then shows the temperature difference to this value directly. Now carefully open the inner vessel (screw cap), add the first substance pellet, and reclose the opening immediately. The temperature first drops slightly and then rises again as soon as the pellet has dissolved. When the value has again become constant, record it together with the exact mass of the pellet. Repeat this procedure for the next portion of the substance. After five concentration steps have been measured, open the pinchcock and switch off the heating. Now remove the inner vessel, dry its outer surface, remove the temperature probe and the pipe; then re-weigh the inner vessel. The mass of the water is now equal to the last measured value less the mass of the empty vessel and the masses of the five substance pellets. For each substance plot the increase in boiling point against the quotient of the mass of the dissolved substance and the mass of water as shown Fig. 2.

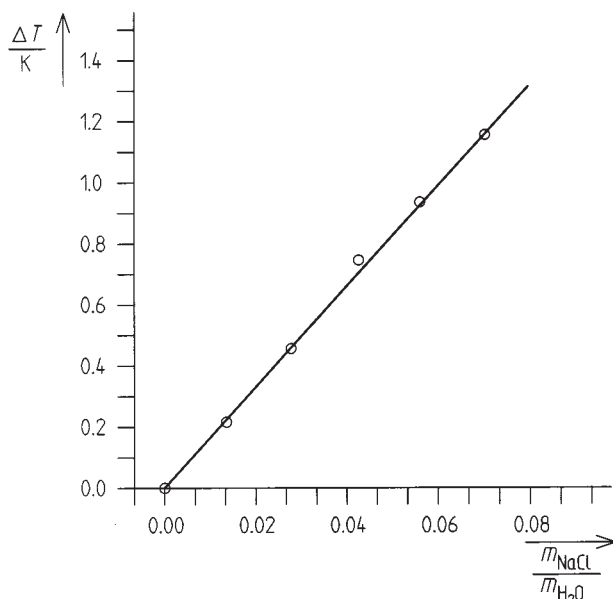


Fig. 2: Example of a measurement: boiling point increase as function of concentration of table salt in an aqueous solution.

### Theory and evaluation

If a small amount of substance B, which has a negligible vapour pressure, is dissolved in a pure solvent A, the depression of the vapour pressure of A can be calculated using Raoult's law - assuming that the solvent demonstrates ideal behaviour. This depression of the vapour pressure is seen in the experiment as an increase in the boiling point of the solution compared with the pure solvent A.

For each equilibrium point, the chemical potential of the vapour phase  $\mu_A^g$  is equal to the chemical potential of the solvent  $\mu_A^l$  ( $\mu_A^g = \mu_A^l$ ). The chemical potential of the solvent in the solution is

$$\mu_A^l = \mu_A^{e1} + RT \ln x_A \quad (1)$$

where  $\mu_A^{e1}$  is the chemical potential and  $x_A$  is the amount of substance of the pure solvent. At boiling point,  $\mu_A^l$  is also equal to the chemical potential  $\mu_A^{g0}$  of the pure solvent vapour.

If  $\mu_A^g = \mu_A^l$ , then the following is obtained:

$$\mu_A^{g0} = \mu_A^{e1} + RT \ln x_A \quad (2)$$

Since the chemical potential of pure substances is identical to the molar free enthalpy  $G^e$ , equation 2 becomes:

$$G_A^{e0} - G_A^{e1} = RT \ln x_A \quad (3)$$

From the Gibbs-Helmholtz equation

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

we can differentiate equation (3) to obtain

$$\frac{H_A^{e1} - H_A^{e0}}{RT^2} = \frac{\Delta_v H}{RT^2} = \frac{d \ln x_A}{dT} \quad (5)$$

The enthalpy of vaporisation  $\Delta_v H$  can be considered 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

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

Since the increase in boiling point  $\Delta T = T - T_0$  is small compared with  $T_0$ , the expression  $TT_0$  can be replaced with  $T_0^2$ . If, at the same time, we consider the amount  $x_B$  of the solute, then  $x_A$  can be replaced with  $1 - x_B$  to obtain:

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

Equation (7) can be developed as a series:

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

If  $x_B$  is small, only the first linear term need be considered. The increase in boiling point is thus

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

For dilute solutions, a good approximation of the amount of substance is the ratio ( $m_B M_A / m_A M_B$ ).  $M_A$ ,  $M_B$  and  $m_A$ ,  $m_B$  are the molar masses and weighed masses of solvent A and solute B, respectively.

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

Finally, the fraction  $m_B M_A / m_A M_B$  can be considered to be equal to  $m/1000$ , where  $m$  is the molality, i.e. the amount of solute in 1000 g of solvent.

$$\Delta T_v = \frac{RT_0^2}{\Delta_v H} \cdot \frac{m}{1000} = K_v \cdot m \quad (11)$$

Constant  $K_v$  is termed the molar elevation of the boiling point or the ebullioscopic constant.

When determining the relative molar mass of a dissolved substance, the fact that the number of free moles  $n_B$  corresponds to the number of free particles must be taken into account. If, however,  $n_B$  moles dissociate into  $z$  smaller particles in solution, then the number of moles actually present becomes

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

where  $\alpha$  is the degree of dissociation.

Under certain conditions, the determination of molar masses using ebullioscopy can therefore only supply the apparent molar mass  $M_s$  which has then to be converted using

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

Similar considerations apply to the associated particles in solution.

### Data and results

$$K_v(\text{water}) = 0.515 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}$$

Molar masses (in  $\text{g} \cdot \text{mol}^{-1}$ ):

NaCl ( $\alpha = 1$ ,  $z = 2$ ): 61.71 (exp.); 58.44 (lit.)

Urea ( $\alpha = 0$ ): 60.83 (Exp.); 60.06 (Lit.)

Hydroquinone ( $\alpha = 0$ ): 108.14 (Exp.); 110.11 (Lit.)