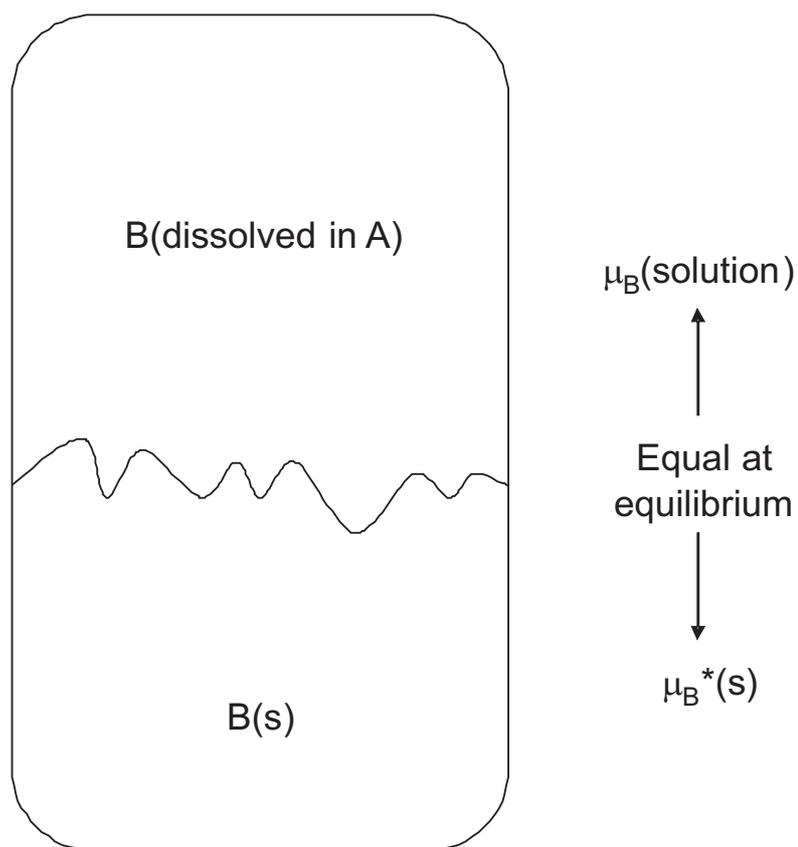


Physical chemistry advanced laboratory course

Temperature Dependence of Solubility

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1 Introduction

In this experiment, the temperature dependence of solubility of succinic acid, $(\text{CH}_2\text{COOH})_2$, in water is studied. From the experimental results, the heat of solution $\Delta_m H_{m,B}$, and the solubility of succinic acid at $T = 298 \text{ K}$ are determined.

2 Theory

Saturated solution

When a solid solute B is left in contact with a solvent A, it dissolves until the solution is saturated. In a saturated solution the undissolved solute is in dynamic equilibrium with the dissolved solute:



When a solid is dissolved, its crystal lattice has to be broken and for this, energy is needed. In so-called ideal dissolution, the energy needed for dissolving is equal to the energy needed for melting the crystal and no other effects that might affect the energy needed are considered. In this exercise, the dissolution of the solute is considered ideal.

Ideal solubility

The ideal solubility can be determined according to the equation (2):

$$\ln x_B = \frac{-\Delta_m H_{m,B}}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right), \quad (2)$$

where $\Delta_m H_{m,B}$ is the heat of fusion of the solute (also called differential heat of solution), T^* is the melting point of the solid solute, T the temperature at which the solubility is measured, and x_B the mole fraction of the solute in solution. According to Eq.(2), the solubility of B decreases exponentially as the temperature is lowered.

The Eq.(2) can also be reformulated in differential form and the mole fraction can be replaced with molality m_S (where S refers to saturated solution):

$$d \ln m_S = \frac{-\Delta_m H_{m,B}}{R} d\left(\frac{1}{T}\right). \quad (3)$$

Thus, the differential heat of solution can be determined from the slope of the curve by plotting $\ln m_S$ as a function of $\frac{1}{T}$.

The solubility is usually reported as molality [mol/kg] or sometimes also as grams per 100 grams of solvent. As the chemical potential in real cases depends on activity rather than on molality, the results are expected to differ from the ideal case.

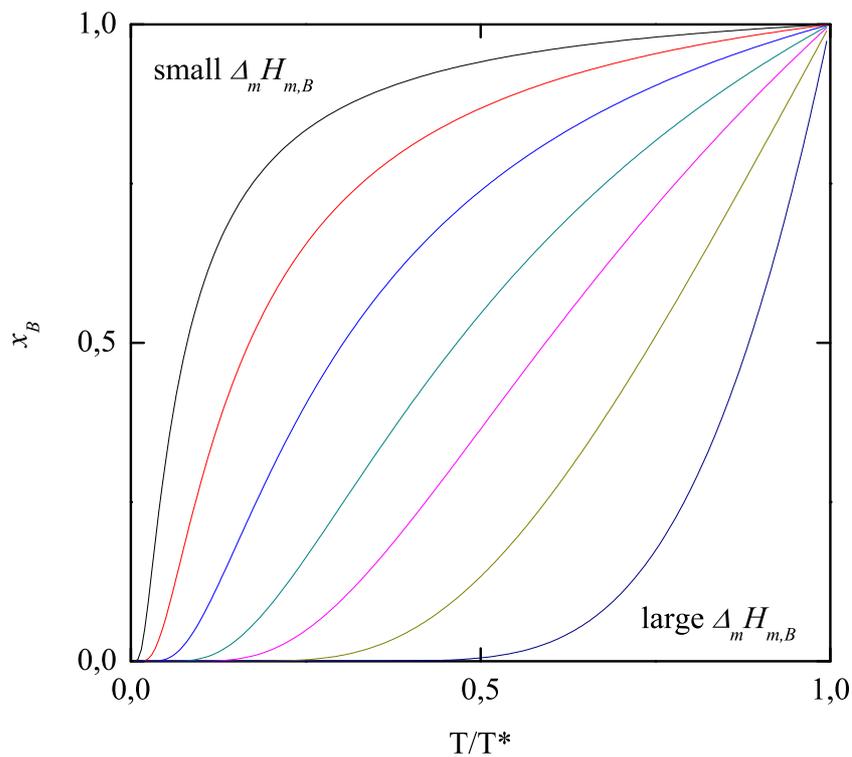


Figure 1: The variation of ideal solubility (the mole fraction of the solute) with temperature. Different curves have different heats of solution.

Partial molar properties and heats of solution

Partial molar properties, such as chemical potential, are intensive properties. The value of a partial molar property Y_m is a sum of components $n_i Y_{m_i}$. According to the Gibbs-Duhem equation, the partial properties of the components are not independent of each other, but $\sum_i dY_{m_i} = 0$. In context of solution enthalpies, the following terminology is used. The mixing enthalpy divided by the amount of substance, $\frac{\Delta H_{mix}}{n_B}$, is designated as the integral heat of solution. The integral heat of solution is the total change in the heat content when a mole of a pure compound is isothermally dissolved in n moles of pure solvent in a final concentration that is generated. The differential heat of solution is defined as

$$\Delta H_{diff,B} = H_{m,B} - H_{m,B}^* = \left(\frac{\Delta H_{mix}}{n_B} \right)_{T,p,n_A}, \quad (4)$$

where the difference in enthalpies in the mixing process is $(H_{m,B} - H_{m,B}^*)dn_B$. The differential heat of solution is the change in the heat content when a mole of a compound is dissolved in such a large amount of solution that the concentration does not change due to the addition.

3 Experimental

In this work, the solubility curve at temperatures between 313–273 K and the differential heat of solution at $T = 298$ K are determined for succinic acid in water.

For a successful experiment it is important that the system is in dynamic equilibrium at all temperatures, so that the solution is saturated and both solid and solution phases are present. This is why you begin your experiment by tempering the saturated solution at $T = 333$ K and by adding solid succinic acid as needed. After this, the measurements are made from $T = 313$ K to lower temperatures at temperature intervals of about ten kelvins. The temperature should be measured with an accuracy of ± 0.1 K. For $T = 273$ K, the system can be tempered in a smaller vessel with ice.

The samples, two for each temperature, are taken with a 10 ml pipette that has been warmed up in a heating chamber that is of slightly higher temperature than the sample. Move the sample directly to a tared 100 ml Erlenmeyer flask and weigh the sample. Titrate the sample in the same flask using 0.5 M NaOH solution and phenolphthalein as an indicator. Remember to take two samples for each temperature to be able to estimate the errors! Check also the concentration of the NaOH solution.

In the measurement log, state the checked concentration of the NaOH solution and the method used for checking, together with the accurate temperatures, and the weighing and titration results with error estimates.

4 Analysis of the results

Collect your results in a table of the following form:

Table 1: Experimental results

Sample	T [K]	$\frac{1}{T} \cdot 10^{-3}$ [K^{-1}]	$m_{solution}$ [g]	NaOH [ml]	m_{acid} [g]
1	313.2	3.193	10.34	57.9	1.645
2			10.29	56.2	1.597
1	etc.
2

Table cont.

Sample	m_{water} [kg]	$\frac{m_{acid}}{m_{water}}$ [g/kg]	m_S	$\overline{m_S}$	$\ln \overline{m_S}$
1	0.008690	189.346	1.603	1.605	0.4731
2	0.008689	189.808	1.607		
1	etc.
2

In the report, show detailed examples of each calculation. Write also down the neu-

trahization reaction and calculate the acid concentration. Plot $\ln \overline{m}_S$ as a function of $\frac{1}{T}$ and determine the slope with its error, from which you can calculate $\Delta_m H_{m,B}$ and its error. Plot m_S [g/kg] as a function of temperature and use the plot to determine the solubility of succinic acid at $T = 298$ K. Compare the result with the literature value.

Discuss also the following questions:

1. What happens when a solid dissolves?
2. What is the difference between differential and integral heat of solution?
3. Estimate the magnitude of the error made when plotting the function as a function of m_S instead of activity.
4. Explain why this method can be used for a relatively poorly soluble compound but not for salts.
5. Why does the solubility of some compounds change considerably as a function of temperature?
6. Discuss how a gas dissolves in a liquid at different temperatures.

References

- [1] Atkins, P. W. and de Paula, J. *Physical Chemistry* (Oxford University Press, Oxford, 2006) 8th edition, pages 153–154.