Dependence of the solubility on temperature

Theoretical background: P.W. Atkins: *Physical Chemistry*, 26.1–3.
Type of practice: Individual.
Purpose of practice: To show that solubility can vary significantly with temperature, and how to obtain thermodynamic data of dissolution (molar dissolution enthalpy and entropy) by determining the solubility of a solid at various temperatures.

1 Introduction

When a solid is in contact with its own solution at a given temperature, thermodynamic equilibrium is sooner or later established in this heterogeneous system, i.e., a saturated solution is formed (if there is enough solid to be dissolved). In this state, the dissolution rate of the solid is equal to the rate of precipitation from the saturated solution (dynamic equilibrium), which is expressed by the equality of the chemical potentials (μ) in thermodynamics,

$$\mu_{\text{solid}} = \mu_{\text{diss}}\,. \tag{1}$$

In an ideal mixture or in a sufficiently dilute solution (where the activity coefficients are one) the chemical potential of the solute can be expressed as a function of the molar fraction (mole fraction):

$$\mu_{\text{diss}} = \mu^0_{\text{diss}} + \mathrm{RT}\ln \mathrm{x}\,, \tag{2}$$

where T is the thermodynamic temperature, R is the gas constant, x is the mole fraction of the dissolved substance, and μ^0_{diss} the standard chemical potential of the dissolved substance, the solute, which is equal to the chemical potential if x=1. This means a non-existing, hypothetical state in which the solute is in a solution without the solvent present. μ^0_{diss} specifies the chemical potential of this state. Equation 2 is true even if the dilute solution is also saturated, so for slightly soluble substances, the combination of Eqs. 1–2 gives

$$\ln \mathrm{x}_{\text{saturated}} = \frac{\mu_{\text{solid}} - \mu^0_{\text{diss}}}{\mathrm{RT}} = -\frac{1}{\mathrm{R}} \cdot \left(\frac{\mu^0_{\text{diss}}}{\mathrm{T}} - \frac{\mu_{\text{solid}}}{\mathrm{T}} \right) \tag{3}$$

where $\mathrm{x}_{\text{saturated}}$ is the mole fraction of the solute in a saturated solution at a given temperature. Eq. 3 is the basis for determining the molar enthalpy of dissolution. However, the equation should be rearranged for the evaluation of the experimental data. To do this, convert the expression μ/T using the following considerations:

By the defining equation of Gibbs energy (earlier it was called free enthalpy, Gibbs free energy, ($\mathrm{G} = \mathrm{H} - \mathrm{T} \cdot \mathrm{S}$, where H is enthalpy and S is entropy)

$$\frac{\mathrm{G}}{\mathrm{T}} = \frac{\mathrm{H}}{\mathrm{T}} - \mathrm{S}\,. \tag{4}$$

The chemical potential is the partial molar Gibbs energy, i.e., the partial derivative of the Gibbs energy according to the amount of a given substance:

$$\mu_{\mathrm{i}} = \left(\frac{\partial \mathrm{G}}{\partial \mathrm{n_i}} \right)_{\mathrm{p,T,n_j}} \qquad (\mathrm{i} \neq \mathrm{j})\ ,$$

where μ_{i} and $\mathrm{n_i}$ is the chemical potential and the amount of substance of the i-th components, p is the pressure, j denotes the other components By this, Eq. 4 can be written as

$$\frac{\left(\frac{\partial \mathrm{G}}{\partial \mathrm{n_i}} \right)_{\mathrm{p,T,n_j}}}{\mathrm{T}} = \frac{\left(\frac{\partial \mathrm{H}}{\partial \mathrm{n_i}} \right)_{\mathrm{p,T,n_j}}}{\mathrm{T}} - \left(\frac{\partial \mathrm{S}}{\partial \mathrm{n_i}} \right)_{\mathrm{p,T,n_j}} \qquad (\mathrm{i} \neq \mathrm{j}),\ \text{so}$$

$$\frac{\mu_\mathrm{i}}{\mathrm{T}} = \frac{\mathrm{H}_\mathrm{m,i}}{\mathrm{T}} - \mathrm{S}_\mathrm{m,i}\,, \tag{5}$$

where $\mathrm{H}_\mathrm{m,i}$ is the partial molar enthalpy and $\mathrm{S}_\mathrm{m,i}$ is the partial molar enthropy of the i-th component. Substituting this into Eq. 3, we get the correlation

$$\ln \mathrm{x}_\mathrm{saturated} = -\left(\frac{\mathrm{H}^0_\mathrm{diss} - \mathrm{H}_\mathrm{m,solid}}{\mathrm{R}}\right)\cdot\frac{1}{\mathrm{T}} + \frac{\mathrm{S}^0_\mathrm{diss} - \mathrm{S}_\mathrm{m,solid}}{\mathrm{R}} \tag{6}$$

This includes partial molar quantities, values that may also be composition dependent due to the derivation according to the amount of substance. However, as with the previous consideration of μ^0_diss, it can be seen that $\mathrm{H}^0_\mathrm{diss}$ and $\mathrm{S}^0_\mathrm{diss}$ are the enthalpy and entropy of one mole solvent-free solute, since they belong to the molar fraction of $x = 1$. By definition, thermodynamic data for a solid should not be composition-dependent, as they relate to a one-component system. For this reason, the partial molar quantities H_m and S_m can be considered simply as molar quantities. After this, it is easy to see that the expression $(\mathrm{H}^0_\mathrm{diss} - \mathrm{H}_\mathrm{m,solid})$ is the difference between the enthalpy of one mole of solute and that of one mole of solid, which is the molar dissolution enthalpy,

$$\Delta\mathrm{H}_\mathrm{dissolution} = \mathrm{H}^0_\mathrm{diss} - \mathrm{H}_\mathrm{m,solid}\,,$$

and the same applies for the entropy

$$\Delta\mathrm{S}_\mathrm{dissolution} = \mathrm{S}^0_\mathrm{diss} - \mathrm{S}_\mathrm{m,\ solid}\,.$$

Substituting those into Eq. 6

$$\boxed{\ln \mathrm{x}_\mathrm{saturated} = -\frac{\Delta\mathrm{H}_\mathrm{dissolution}}{\mathrm{R}}\cdot\frac{1}{\mathrm{T}} + \frac{\Delta\mathrm{S}_\mathrm{dissolution}}{\mathrm{R}}} \tag{7}$$

Based on this, by plotting the natural logarithm of the molar fraction of the saturated solution as a function of the reciprocal of the thermodynamic temperature, a line is obtained from which the molar dissolution enthalpy and the molar dissolution entropy can be calculated.

It should be noted that the relationship defined by Eq. 7, gives a straight line if the value of the heat of dissolution and the entropy of dissolution are independent of temperature. Experience has shown that this is true (within the experimental errors) for small temperature changes (few times of 10 degree), which can also be seen from the following consideration: The heat of dissolution is essentially the difference between the lattice energy of the solid and the solvation energy of the solute. As the temperature increases, less energy is needed to break up the crystal lattice, but solvation also means less energy gain. Because of this, the enthalpy change resulting from the two processes is usually much less temperature dependent than the two enthalpy changes separately. The change in entropy by dissolution is also basically the result of two processes. Disintegration of the crystal lattice of the solid results in a large increase in disorder, thus entropy, while the formation of a solvation sphere increases the ordering of the solvent, thus leading to a decrease in entropy. As the temperature increases, the absolute value of the entropy change in both processes decreases, so their sum can be considered constant over a smaller temperature range, similar to enthalpy.

2 Experimental

In the practice, the thermodynamic data characterizing the dissolution of benzoic acid in water are determined. Make saturated benzoic acid solutions in the temperature range of 25 – 50 °C, and take samples of the solution at given temperatures, and determine the amount of benzoic acid in it by titration with NaOH using phenolphthalein indicator.

First, 500 cm^3 solution of 0.015 – 0.025 M NaOH should be prepared by measuring solid NaOH. Unless the instructor says otherwise, the concentration of the NaOH solution is 0.02 M. The exact concentration of the NaOH solution ($\mathrm{c_b}$) should be determined. To do this, titrate 3 cm^3 of the available acetic acid solution of known concentration (~0,1 M) and from the titration data, calculate the exact value of c_b. Then a saturated benzoic acid solution is prepared from ~130 cm^3 distilled water at ~50 °C. For that, warm the water in a 250 – 300 cm^3 beaker between 55 – 60 °C, add enough solid benzoic acid (5 – 7 g) that after stirring the solution for ten minutes, at least 1 – 2 g of solid remains [1]. The temperature of the solution is kept between 55 – 60 °C throughout the stirring period. You may also use the acid-water mixture left over from the previous practices, and you may use that container after your practice for your remaining solution, as well. The benzoic acid solution is prepared in this way because the saturation concentration is reached slowly when the solution is stirred only at 50 °C. At higher temperatures, more benzoic acid dissolves relatively quickly. Upon cooling the solution, the excess benzoic acid precipitates (i.e., no supersaturated solution is formed) if the solution is stirred vigorously and there is a lot of solid benzoic acid in the solution (no nucleation is required). Then the solution is let to slowly cool down, and samples are taken from it at given temperatures. Before sampling, clean the available Erlenmeyer or titration flasks and fill the burette with NaOH solution.

When the temperature of saturated benzoic acid reaches 50 °C, sampling begins. Samples are taken with a 5 cm^3 syringe by pulling an 8 – 10 cm long plastic tube onto the tip of the syringe and placing cotton wool at the end of the tube so that the syringe only draws in the saturated solution, not the solid. The best way to do this is to press about one-third of the used cotton wool swab ~ 0.5 cm deep into the end of the tube and spread two-thirds of the cotton wool outside the tube. The end of the swab is placed in the saturated solution and the sample is aspirated with the syringe plunger. Be careful not to suck too hard, as the cotton wool can be easily sucked into the tube. At about half of the sampling, read the exact temperature (with an accuracy of 0,1 °C). This value will be used later in the evaluation. After taking the sample, the tube is removed from the end of the syringe and the sample is put into a pre-weighed flask and weigh its mass. The syringe is filled once with distilled water, which is also added to the sample. Its mass does not need to be measured. There are two reasons for adding distilled water. On one hand, the syringe is washed and, on the other hand, the sample is diluted. The latter is especially important at higher temperatures because, without dilution, solid benzoic acid precipitates on cooling. This solid is difficult to redissolve during titration, making it difficult to work with. The plastic tube is then washed, put back onto the syringe, and a new cotton swab is inserted for the next sampling. The samples taken are titrated with NaOH solution as soon as possible. While cooling and stirring the benzoic acid solution, take samples at about 2 °C temperature change and titrate. Flasks of samples already titrated can be washed, which is also necessary if there are fewer flasks than the number of samples. A total of 13 samples are taken, so the temperature of the last sample is ~26 °C. Upon completion of the measurements, the mixture of residual benzoic acid solution and solid benzoic acid must be poured into a collecting container so that it can be used in the following practice.

3 Evaluation

- From the titration of the acetic acid solution of known concentration, calculate the exact concentration of the NaOH solution: $c_{\text{acetic acid}} =$ .... M and $c_b =$, ... M.
- Summarize the molar masses, the measured data and the calculated results according to Table 1. In the table, t is the temperature of the sample in Celsius degree, V_{base} is the volume of NaoH consumed in the titrations, m is the corresponding mass and n is the corresponding amount of substance.

Table 1: Summary of the data.

$M_r(H_2O)$= ...., M_r(benzoicacid)= ....

t (°C)	T (K)	m_{sample} (g)	V_{base} (cm^3)	$n_{\text{benzoic acid}}$ (mol)	$m_{\text{benzoic acid}}$ (g)	...
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[1] It is enough to estimate the amount of solid.

...	m_{water} (g)	n_{water} (mol)	$molality_{benzoic\ acid}$ (mol/kg)	$x_{saturated}$	$\ln x_{saturated}$	1/T (1/K)
...						

- Using the data in the table, plot the molality of saturated benzoic acid as a function of temperature in degrees Celsius and analyze the figure in one or two sentences (e.g., how and to what extent solubility changes with temperature).
- Based on the data in the table, and using Eq. 7, make a graph of $\ln x_{saturated}$ - 1/T, fit a straight line to the points, and calculate the molar dissolution enthalpy and entropy of benzoic acid and standard deviations of those, as well (see Appendix). Analyze the values of the results, how appropriate, realistic, etc. they can be!

Control question

1. What is the general condition for thermodynamic equilibrium?
2. How can the chemical potential of a solute be expressed in an ideal or sufficiently dilute solution?
3. Explain the meaning of μ^0_{diss} in max. three sentences.
4. Give the relationship between chemical potential and Gibbs energy (free enthalpy)!
5. Explain in 3 – 4 sentences why the partial molar quantities characterizing the dissolution process can be replaced by simple molar quantities!
6. Define the enthalpy and entropy of dissolution!
7. Give the relationship used to calculate the thermodynamic parameters of the solution from the experimental data!
8. What processes result in the enthalpy and entropy change connected to dissolution of a solid?
9. How do you make a saturated benzoic acid solution at 50 °C?
10. How do you ensure that the solution is not supersaturated at a given temperature?
11. How do you ensure that there are no solid particles in the sample to be titrated?
12. How can you determine the exact mass of the samples to be titrated?
13. A sample of 4.935 g was taken from the saturated benzoic acid solution and titrated with 0.0431 M NaOH solution. The equivalence point was reached at 15.72 cm^3. What was the molar fraction of benzoic acid (C_6H_5COOH) in the titrated sample? $A_r(H) = 1.01$, $A_r(C) = 12.01$ and $A_r(O) = 16.00$.
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