Physikalische-Chemisches Praktikum für Anfänger

Skript for Experiment

A09

Phase Diagram of a Eutectic Binary Mixture

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1 Objective

The x-T-phase diagram of $LiNO_3$-$NaNO_3$ has to be measured employing cooling curves. Using a simple Ansatz the phase diagram will be calculated and compared to the experimental one.

2 What you should know

Equilibrium conditions for phase equilibria; concentration dependence of $\Delta_{mix}H$, $\Delta_{mix}V$, $\Delta_{mix}G$ and $\Delta_{mix}S$ of ideal mixtures; colligative phenomena; experimental methods for the determination of the activity.

3 Basics

3.1 Equilibrium conditions for binary phase diagrams

Besides the conditions for the thermal and the mechanical equilibrium between two phases α und β

$$\text{thermal equilibrium:} \qquad T(\alpha) = T(\beta) \tag{1}$$

$$\text{mechanical equilibrium:} \qquad p(\alpha) = p(\beta) \tag{2}$$

the conditions for the chemical equilibrium of both components A and B in both phases have to be fulfilled, this means:

$$\mu_A(\alpha) = \mu_A(\beta) \quad \text{and} \quad \mu_B(\alpha) = \mu_B(\beta) \,. \tag{3}$$

Repeating basic knowledge: the chemical potentials μ_A and μ_B are also known as the partial molar enthalpies of components A and B. They are defined as follows:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} \,. \tag{4}$$

Thus, at constant temperature and pressure we have for a binary system:

$$\mathrm{d}G = \left(\frac{\partial G}{\partial n_A}\right)_{T,p,n_B} \mathrm{d}n_A + \left(\frac{\partial G}{\partial n_B}\right)_{T,p,n_A} \mathrm{d}n_B = \mu_A \mathrm{d}n_A + \mu_B \mathrm{d}n_B \,. \tag{5}$$

If the activity a_i of component i is known as function of the mole fraction x_i and the temperature T in phase α ($a_i = a_i(\alpha;\, x_i,\, T)$), the chemical potential of this component, $\mu_i(\alpha;\, x_i,\, T)$, can be calculated choosing an appropriate reference state. A possible reference state can be the chemical potential of the pure component $\mu_i^*(\alpha;\, T)$.

$$\mu_i(\alpha;\, x_i, T) = \mu_i^*(\alpha;\, T) + RT \ln\left(a_i(\alpha;\, x_i, T)\right) \,. \tag{6}$$

According to the Gibbs-Duhem equation

$$\sum_{i=A,B} x_i \mathrm{d}\mu_i = 0 \tag{7}$$

the partial molar quantities can not be chosen independently. In principle, integrating the Gibbs–Duhem equation μ_B can be calculated from μ_A. The integral molar free enthalpy is then:

$$G_m(\alpha;\, x_A, T) = x_A \mu_A(\alpha;\, x_A, T) + (1 - x_A)\mu_B(\alpha;\, x_A, T)\,. \tag{8}$$

3.2 Calculating the eutectic phase diagram

In this laboratory experiment the phase diagram of $LiNO_3$-$NaNO_3$ (A: Lithium nitrate, B: Sodium nitrate) will be investigated. The solids of both components do not mix in the entire composition range. The liquidus curves start at the melting points of both components and fall with the addition of the respective second component. They meet at the eutectic point. Here, three phases are in thermodynamic equilibrium: pure solid $LiNO_3$, pure solid $NaNO_3$ and a liquid mixed phase with the eutectic composition. In some cases phase diagrams of this kind can be constructed quite easily by calculating the freezing depression curves of both components (colligative phenomenon).

Starting point for this calculation is the equilibrium of pure solid A with a liquid phase consisting of A and B. Thus, we have at constant temperature T:

$$\begin{aligned} \mu_A(s;\, T) = \mu_A^*(s;\, T) = \mu_A(l;\, T) &= \mu_A^*(l;\, T) + RT\ln(a_A(l;\, T))) \\ \Rightarrow \quad \frac{\mu_A^*(s)}{T} - \frac{\mu_A^*(l)}{T} &= R\ln(a_A(l))\,. \end{aligned} \tag{9}$$

Employing the Gibbs-Helmholtz equation

$$\mathrm{d}\left(\frac{\mu}{T}\right) = \left(\frac{\partial(\mu/T)}{\partial T}\right)_p \mathrm{d}T = \left(\frac{\partial(G_m/T)}{\partial T}\right)_p \mathrm{d}T = -\frac{H_m}{T^2}\mathrm{d}T \tag{10}$$

one finds at p =const.:

$$\mathrm{d}\left(\frac{\mu_A^*(s)}{T}\right) - \mathrm{d}\left(\frac{\mu_A^*(l)}{T}\right) = R\,\mathrm{d}\ln(a_A(l)) = -\frac{H_{A,m}^*(s)}{T^2}\mathrm{d}T + \frac{H_{A,m}^*(l)}{T^2}\mathrm{d}T\ , \tag{11}$$

which rearranges to:

$$\mathrm{d}\ln(a_A(l)) = \frac{H_{A,m}^*(l) - H_{A,m}^*(s)}{RT^2}\mathrm{d}T = \frac{\Delta_{melt}H_{A,m}^*}{RT^2}\mathrm{d}T\ . \tag{12}$$

So far we only assumed that the solubility of the respective second component in the pure solid can be neglected. For the integration of equation (12) we have to assume further on that the melting enthalpies of the pure components (here of A: $\Delta_{melt}H^*_{A,m}$) are independent of temperature.

$$\int\limits_{a_A(l)=1}^{a_A(l)} \mathrm{d}\ln(a_A(l)) = \int\limits_{T^*_{f,A}}^{T} \frac{\Delta_{melt}H^*_{A,m}}{RT^2}\mathrm{d}T \approx \frac{\Delta H^*_{A,m}}{R} \int\limits_{T^*_{f,A}}^{T} \frac{\mathrm{d}T}{T^2} \tag{13}$$

$$\ln(a_A(l)) = \frac{\Delta H^*_{A,m}}{R}\left(\frac{1}{T^*_{f,A}} - \frac{1}{T}\right) . \tag{14}$$

Our third approximation is more severe: we assume that Raoult's law is valid, i. e., we apply the law of the ideal mixture and set the activity coefficient γ_A in the whole compositional range equal to one: thus, $a_A(l) \approx x_A(l)$

$$\ln\left(x_A(l)\right) = \frac{\Delta H^*_{A,m}}{R}\left(\frac{1}{T^*_{f,A}} - \frac{1}{T}\right) = \frac{\Delta H^*_{A,m}}{R}\left(\frac{1}{T^*_{f,A}} - \frac{1}{T(x_A)}\right) . \tag{15}$$

T in equation (15) is the liquidus temperature at composition x_A. At this temperature a solid phase starts to precipitate from the liquid. Reorganizing (15) one finds the liquidus temperature as function of x_A:

$$T(x_A) = \left(\frac{1}{T^*_{f,A}} - \frac{R\ln(x_A(l))}{\Delta_{melt}H^*_{A,m}}\right)^{-1} . \tag{16}$$

The same holds for component B:

$$T(x_B) = \left(\frac{1}{T^*_{f,B}} - \frac{R\ln(x_B(l))}{\Delta_{melt}H^*_{B,m}}\right)^{-1} = \left(\frac{1}{T^*_{f,B}} - \frac{R\ln(1-x_A(l))}{\Delta_{melt}H^*_{B,m}}\right)^{-1} .$$

Starting from pure A and B one can plot the liquidus curves in the phase diagram. At the intersection one finds the eutectic point, definded by the eutectic composition, $x_{A,eut}$, and the eutectic temperature, T_{eut}.

3.3 Experimental determination of a phase diagram

Phase diagrams can be determined quite easily applying cooling curves. A homogeneous phase cools down according to an exponential time law. Passing a phase transition the latent heat leads to more or less distinct discontinuities in the cooling curves. This is shown schematically in figure 1.

4 Experimental Part

The experimental set up is quite simple (fig. 2, left): A test tube (∅ ≈ 10 mm) is filled with not much more than 0,5 g of the sample substance. It is mounted in the fume hood on a laboratory stand with a clamp. A mantle thermocouple is inserted in the test tube close to the bottom without touching the glass wall. The salt mixture can be heated with a Bunsen burner.

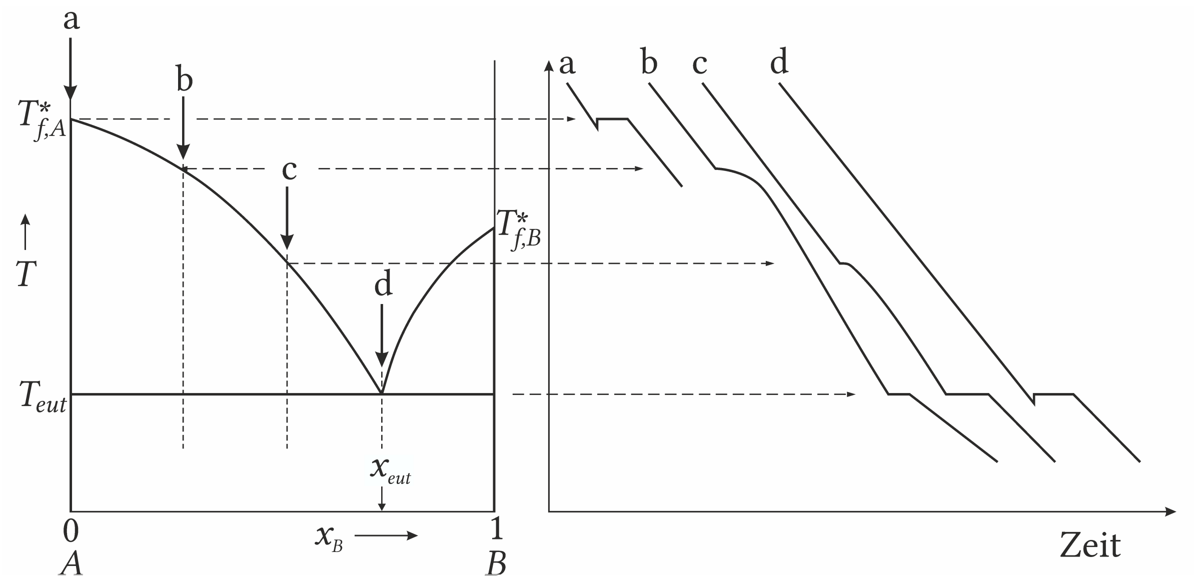

Fig. 1: Typical shape of a eutectic phase diagram. It is characterized by complete miscibility of the components in the liquid phase and by complete immiscibility in the solid state below the eutectic temperature. In the triangular shaped phase regions the pure solid, *A* or *B*, coexists with a liquid phase consisting of both A and B. The shape of the respective cooling curves (a to d) is shown in the right panel.

Measurement of the temperature: The temperature is measured by a digital multimeter (e. g. type M-4660A) connected to personal computer via the serial port (RS 232). The yellow plug of the thermocouple has to be connected to the mulitmeter (yellow framed connectors). Switch on the mulitmeter. Start the program *Cosigraph 2*. Use the left mouse buttons to drop the objects “Gerät”, “Tabelle” and “Diagramm” from the object library (“Konfigurationsobjekte”) into the empty window on the right side. Point to “Gerät” and set in the window “Eigenschaften” the model of the multimeter (Metex 4660A). Now point to “Tabelle” and open unter “Input” a new window. Under “Verfügbare Objekte” “Device1” can be moved to the right window using the »-key. Acknowledge with “Ok”. Repeat the procedure with the diagram. “Device1”, “Tabelle2” and “Graph3” are now connected with arrows. Under “Datei” the multimeter has to be connected to the thermocouple. The measurement starts by clicking ▶. Double clicking “Device”, “Table” und “Graph” the multimeter reading appears as sequence of numbers or as a graph versus time. Using ■ the measurement is stopped. The data can be exported to a file int the window “Tabelle”.

Experimetal procedure: Preprare 8 samples $(NaNO_3)_x(LiNO_3)_{1-x}$ with mole fractions from $x = 0$ to $x = 1$ and fill it into the test tubes. The mass of each sample should not exceed 0,5 g.

Adjust a test tube in the clamp of the lab stand as shown in fig. 2. The tip of the

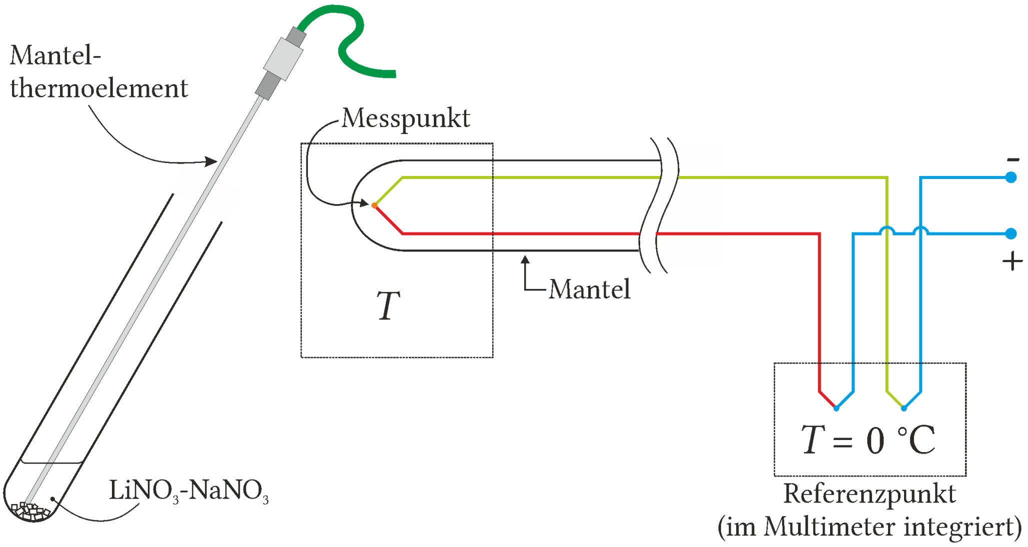

Fig. 2: Left: experimental set up with test tube, sample and mantle thermocouple. Right: schematic sketch of the thermocouple. The temperature is measured at the tip formed by the welding point contacting both thermocouple alloys. For insulation the mantle is filled with Al_2O_3-powder. The contact of the thermo wires (green and red) with the copper wire (blue) is set to 0 °C. In this experiment we use a thermocouple of Type K, consisting of a NiCr-alloy ("Chromel") as positive pole and a NiAl-alloy ("Alumel") as the negative pole. The thermopower is approximately 40 μV/K. In modern multimeters the reference point is located in the measuring device. The thermopower to temperature is calculated by the multimeter.

thermocouple should be well inserted in the sample without touching the glass walls. Liquify the sample with the torch without heating too much above 500 °C (nitrates may decompose). The salt samples are a bit hygroscopic and gas bubbles may develop. This improves the mixing process and leads to a homogeneous mixture.

As the entire sample is homogeneous and liquid the cooling process has to be recorded well below the eutectic temperature (how can this temperature be determined in an effective way?). Record two or three cooling cycles for one sample until they are reproducible. The heating and cooling cycles of a sample should be stored in a single file. Use the ".txt"-format and select a subdirectroy e. g. "Eigene Dateien\WS1819\Group-No". Copy the data on a USB-memory-stick for further analysis.

5 Data evaluation

1. Determine the melting points of the pure components $LiNO_3$ and $NaNO_3$. Compare your results with literature data. Is the solid-solid phase transition in $NaNO_3$ discernible in the cooling curve?

2. Determine the temperature of the liquidus curve and the eutectic temperature. Construct the phase diagram.
3. According equation (16) calculate the phase diagram and plot these results together with your experimental data points.
4. Estimate the accuracy of the phase transition temperatures and the compositions in your experiment. Calculate and draw error bars in the graphical representation of the phase diagram.
5. How does the calculated phase diagram compare to the measured data points? Is a possible disagreement significant and systematic? If yes, what can be concluded?

6 Data and literature

Substanz	$\frac{T_f^*}{\mathrm{K}}$	$\frac{T_f^*}{^\circ\mathrm{C}}$	$\frac{\Delta_{melt}H_m^*}{\mathrm{kJ/mol}}$
$LiNO_3$	525	252	25,61
$NaNO_3$	580	307	14,73

Literature: Janz 1967

1. H. Okamoto und T. B. Massalski (Editor), *Phase Diagrams of Binary Gold Alloys*, ASM Interantional, Metals Park (Ohio, USA) 1897.
2. G. J. Janz, *Molten Salt Handbook*, Academic Press, New York, 1967.

7 Suggestions for the preparation of this experiment

Calculate a weighing list with the approximate amounts of $LiNO_3$ and $NaNO_3$, respectively. Boundary condition: the overall mass should be in the interval between 0,4 g and 0,6 g. The compositions of the samples should be uniformly distributed in the entire mole fraction range. Try to plot the phase diagram according equation (16).

8 Hints for the risc assessment

- Think of the Bunsen burner,
- the chemicals (usage and disposal),
- decomposition of nitrates (what may develop in this case?),
- all the rules for IT-safety.