ЛАБОРАТОРИЯ ХИМИЧЕСКОЙ ТЕРМОДИНАМИКИ

МОСКОВСКИЙ ГОСУДАРСТВЕННЫЙ УНИВЕРСИТЕТ имени М.В. ЛОМОНОСОВА

Определение фазовых границ двухкомпонентных систем методом ДСК

н.с., к.х.н. Белова Е. В.

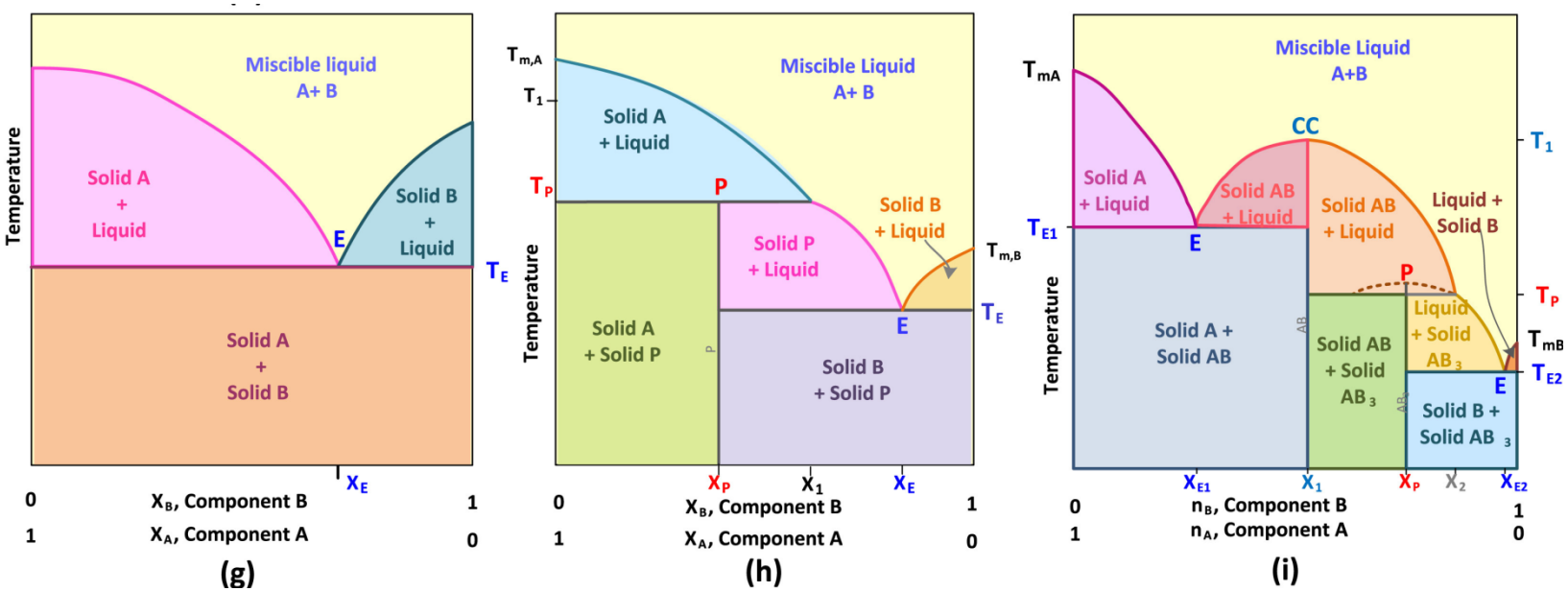
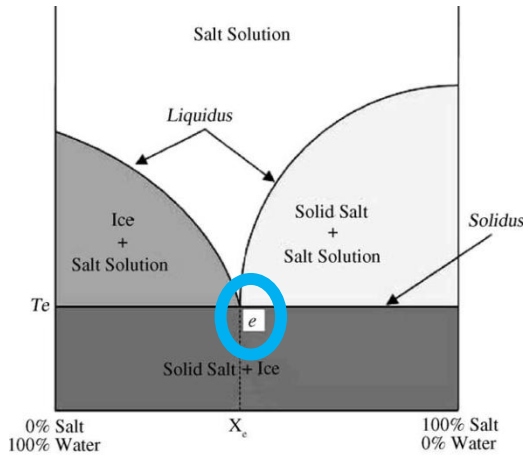
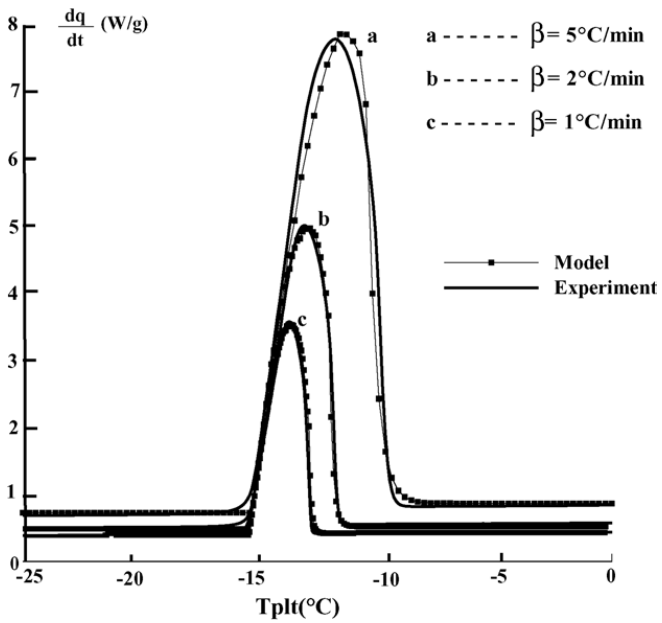


Рис. из 10.1016/j.rser.2017.01.108

Случай диаграммы с простой эвтектикой – что мы не рассказываем на практикуме?

Предсказание кривых ДСК





1. Разбиение ячейки на «конечные объёмы»
2. Запись уравнения теплообмена (на **ЧТО** идет тепло)

Теплоёмкость раствора **Доля расплавившегося льда**

$$\rho c_p \frac{\partial T}{\partial t} = \lambda \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \right) - \rho_g A \frac{\partial X_g}{\partial t}$$

Плотность раствора **Теплопроводность раствора**

$$A = L_F + \left(\frac{X_e}{1 - X_e} \right) L_D$$

Энтальпия плавления льда **Теплота растворения соли в эвтектической смеси**

Jamil, A., Kousksou, T., Zeraouli, Y., Gibout, S., & Dumas, J. P. (2006). Simulation of the thermal transfer during an eutectic melting of a binary solution. *Thermochimica Acta*, *441*(1), 30-34.

Теплообмен и граничные условия

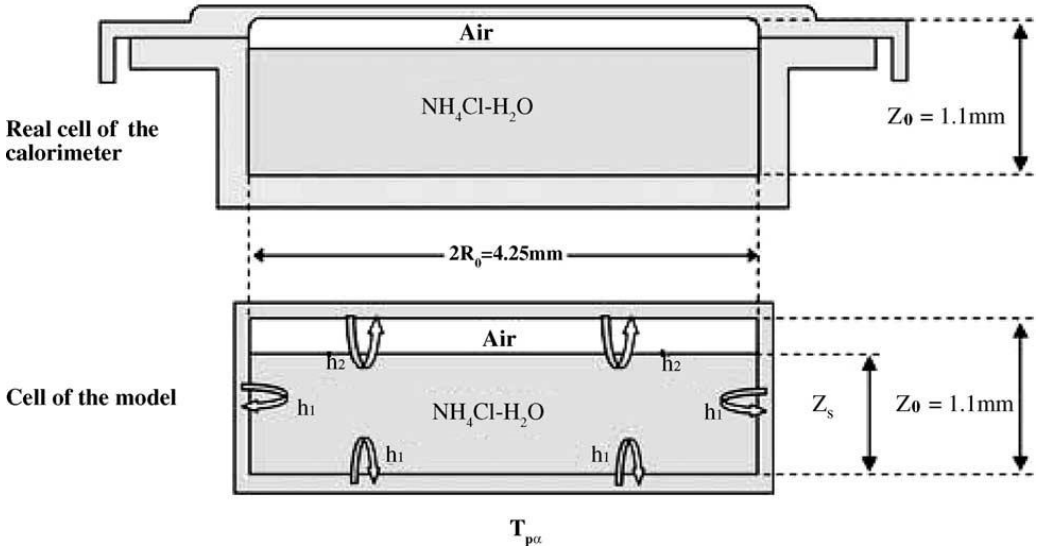
$$\left(\frac{\partial T}{\partial r}\right)_{r=0} = 0$$

$$-\lambda\left(\frac{\partial T}{\partial r}\right)_{r=R} = h_2(T - T_{\mathrm{plt}})$$

$$-\lambda\left(\frac{\partial T}{\partial z}\right)_{z=0} = h_2(T - T_{\mathrm{plt}})$$

$$-\lambda\left(\frac{\partial T}{\partial z}\right)_{z=Z} = h_1(T - T_{\mathrm{plt}})$$

Образец передаёт тепло тиглю



$$T_{\mathrm{plt}} = \beta t + T_0$$

$$X_{\mathrm{g}}(r, z, 0) = 0$$

В нач. момент $t = 0$

Тигель отдает тепло через нижнюю грань контактной площадке

$$\frac{\mathrm{d}q}{\mathrm{d}t} = -\Sigma_i h_i (T_i - T_{\mathrm{plt}}) \Delta S_i$$

Jamil, A., Kousksou, T., Zeraouli, Y., Gibout, S., & Dumas, J. P. (2006). Simulation of the thermal transfer during an eutectic melting of a binary solution. *Thermochimica Acta*, *441*(1), 30-34.

Интегрирование по образцу

$$\rho c_p \frac{\partial T}{\partial t} = \lambda \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \right) - \rho_g A \frac{\partial X_g}{\partial t}$$

Для каждого i-ого «кольца»

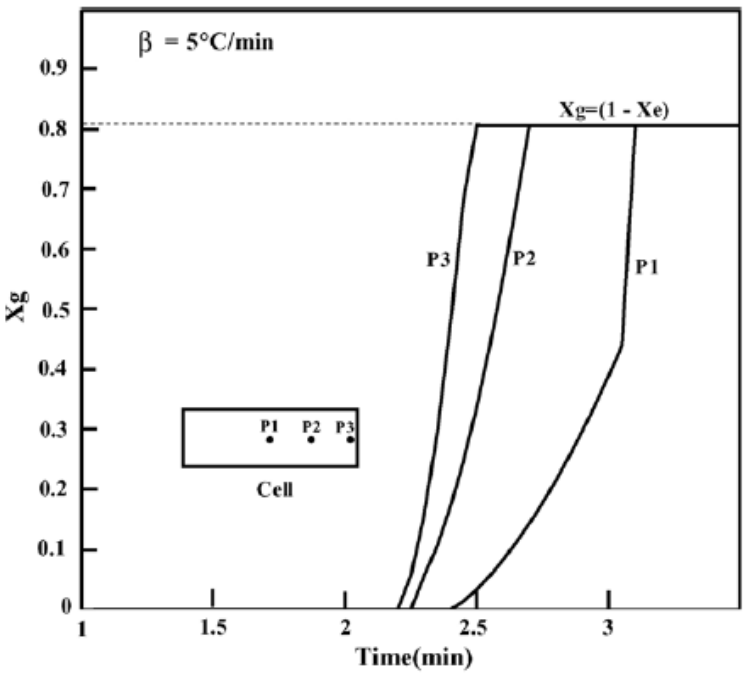


Fig. 9. X_g versus radius for $\beta = 5\,°C/min$.

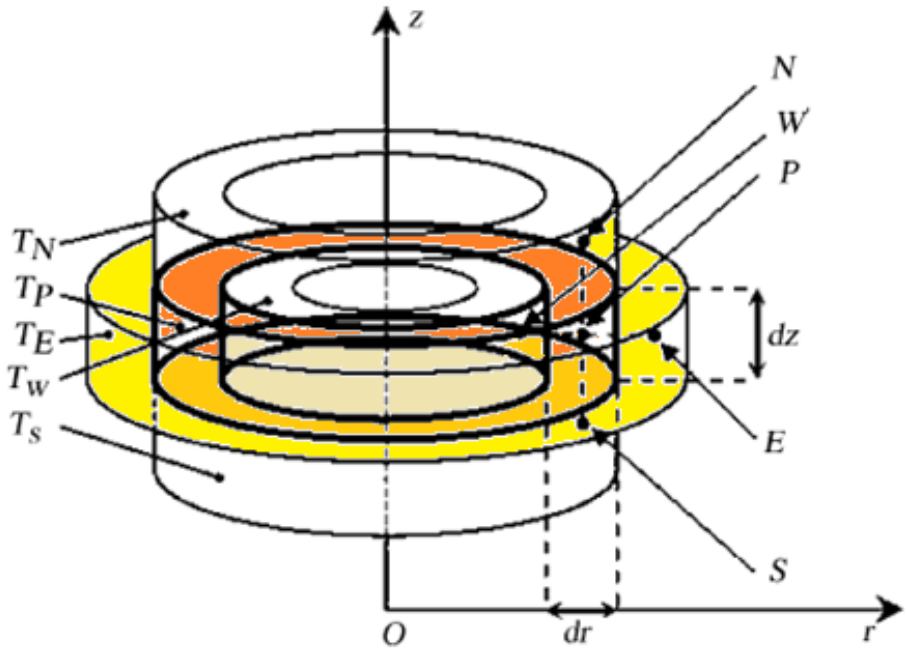


Fig. 5. Control volume.

Jamil, A., Kousksou, T., Zeraouli, Y., Gibout, S., & Dumas, J. P. (2006). Simulation of the thermal transfer during an eutectic melting of a binary solution. *Thermochimica Acta*, *441*(1), 30-34.

Температура в ячейке

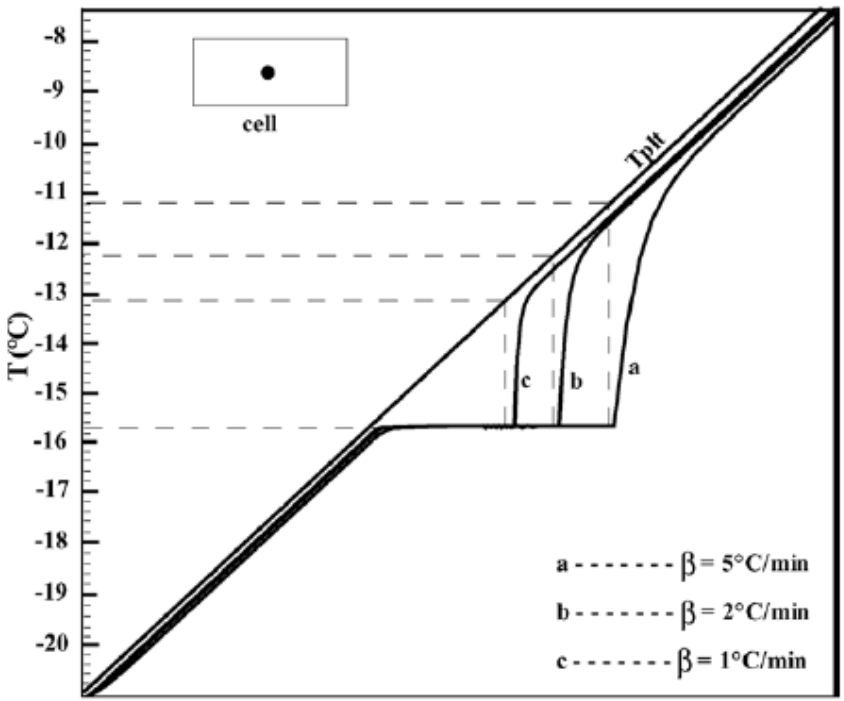


Fig. 10. Influence of ß on the temperature in the center of the sample

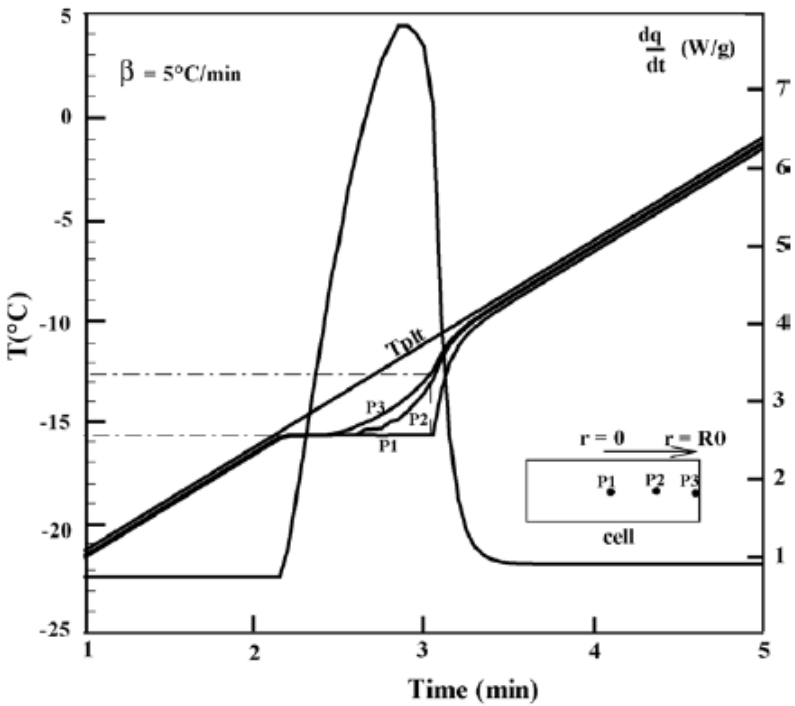
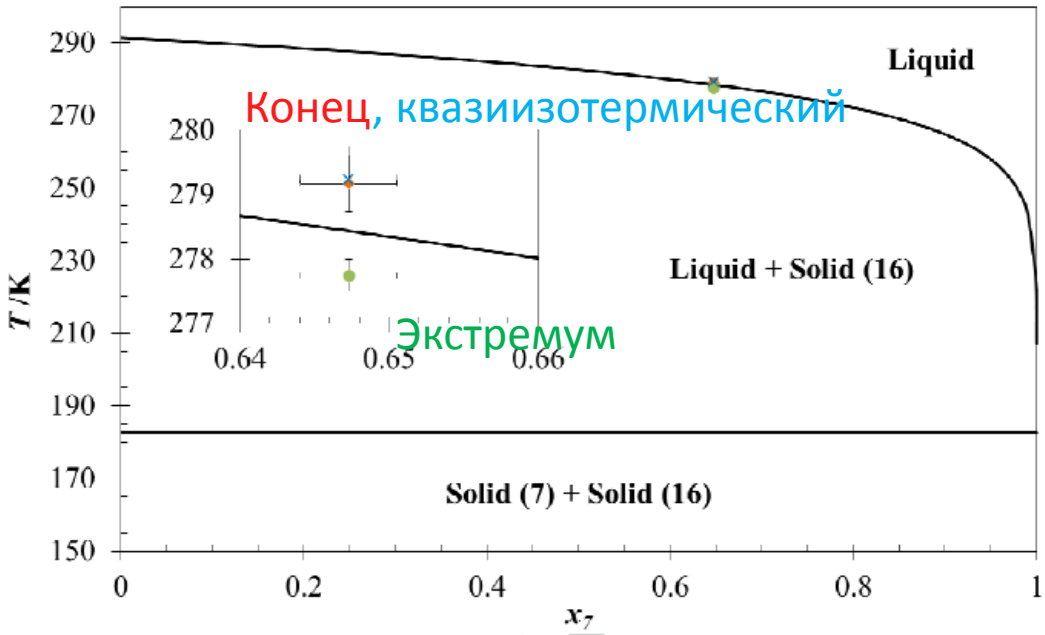


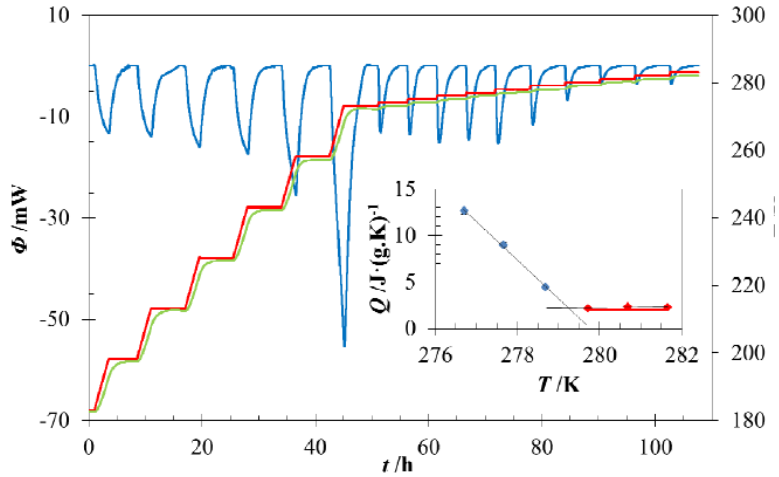
Fig. 8. Temperature versus radius for $\beta = 5\,^{\circ}$C/min.

Jamil, A., Kousksou, T., Zeraouli, Y., Gibout, S., & Dumas, J. P. (2006). Simulation of the thermal transfer during an eutectic melting of a binary solution. *Thermochimica Acta*, *441*(1), 30-34.

Ликвидус. T_{peak} или T_{end}?

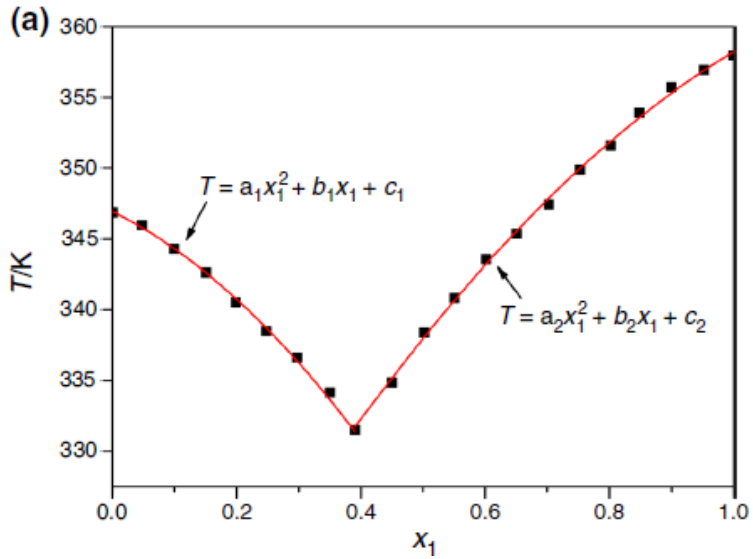
Скорости сканирования в данной работе меньше 0. 1 К/мин!

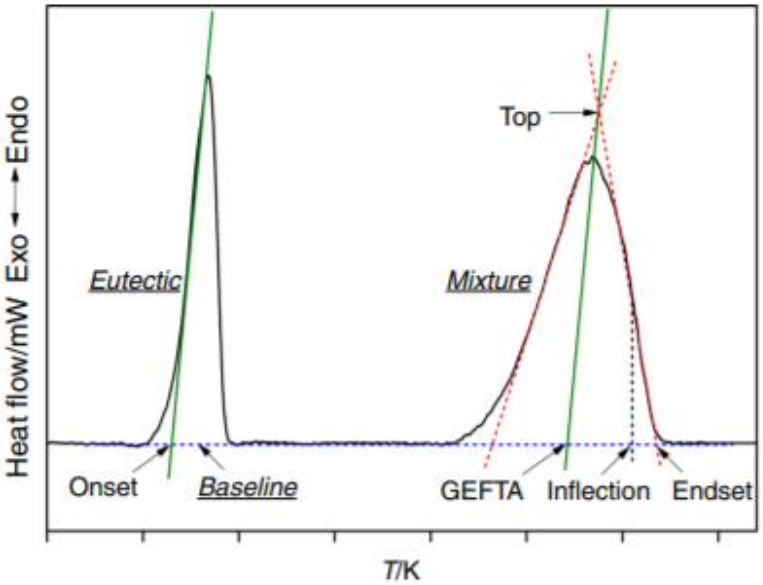




Oakley, J. H. et al. (2017). Determination of melting temperatures in hydrocarbon mixtures by differential scanning calorimetry. The Journal of Chemical Thermodynamics, 108, 59-70.

Ликвидус: T_{peak} или T_{end}?





Характ.	β=0 К/мин		β=1 К/мин	
	Система 1	Система 2	Система 1	Система 2
top	0.849	0.887	0.708	0.749
GEFTA	0.269	0.360	0.190	0.290
Inf	0.933	1	0.850	1
End	0.828	0.920	0.533	0.690

ТЕСТ на согласованность данных (Consistency)

Chelouche, S. et al. (2020). Suitable temperature assignment for liquidus line in SLE investigation by DSC. Journal of Thermal Analysis and Calorimetry, 139(1), 475-487.

Симуляция ликвидуса

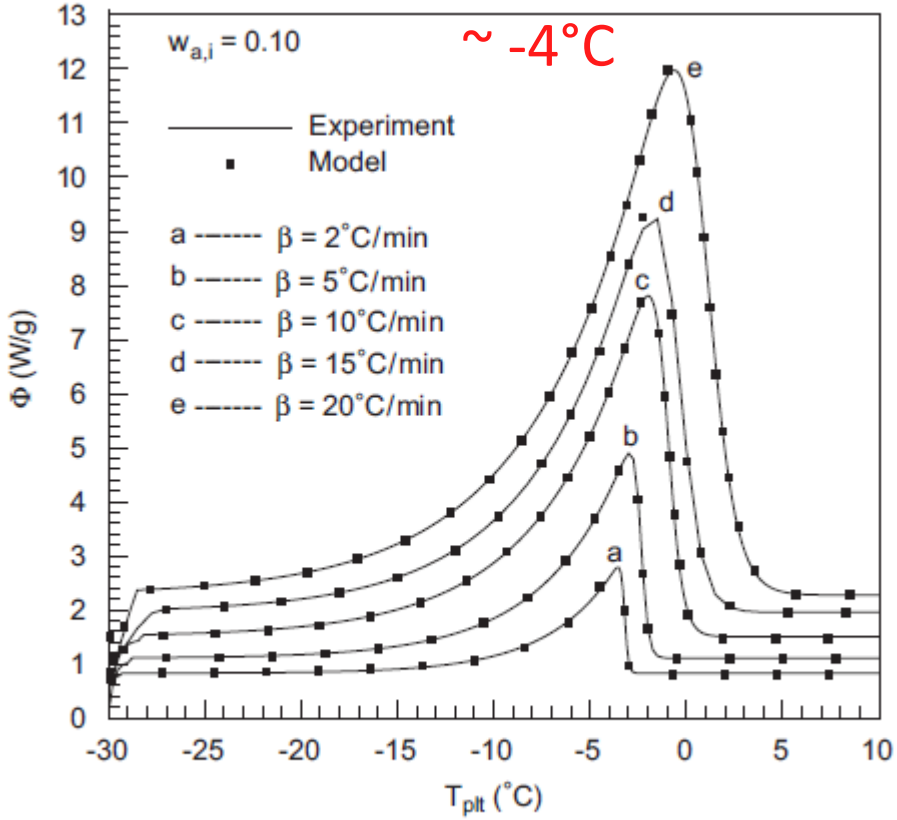


Fig. 3. Effect of the heating rate on the shape of thermograms.

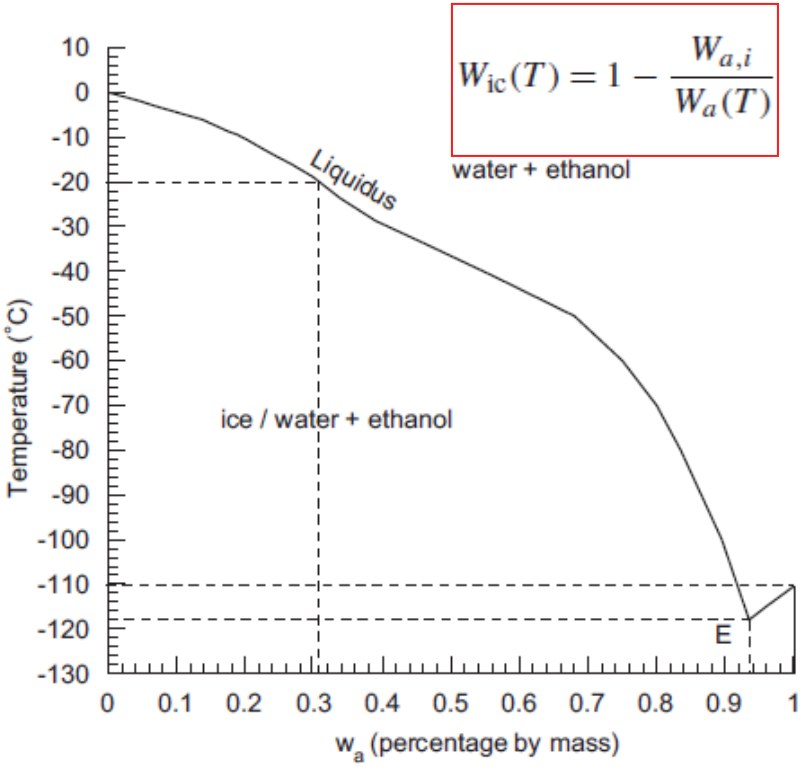


Fig. 1. Phase diagram of the aqueous binary solution of ethanol.

Kousksou, T., Jamil, A., Zeraouli, Y., & Dumas, J. P. (2007). Equilibrium liquidus temperatures of binary mixtures from differential scanning calorimetry. *Chemical Engineering Science*, *62*(23), 6516-6523.

Исчезновение твердого вещества

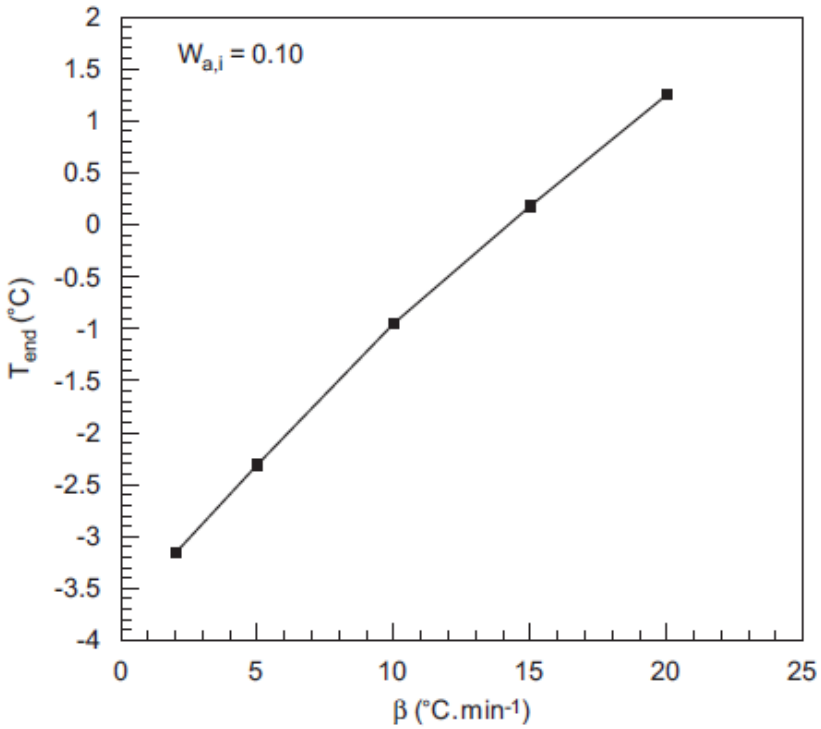


Fig. 6. T_{end} for different heating rate.

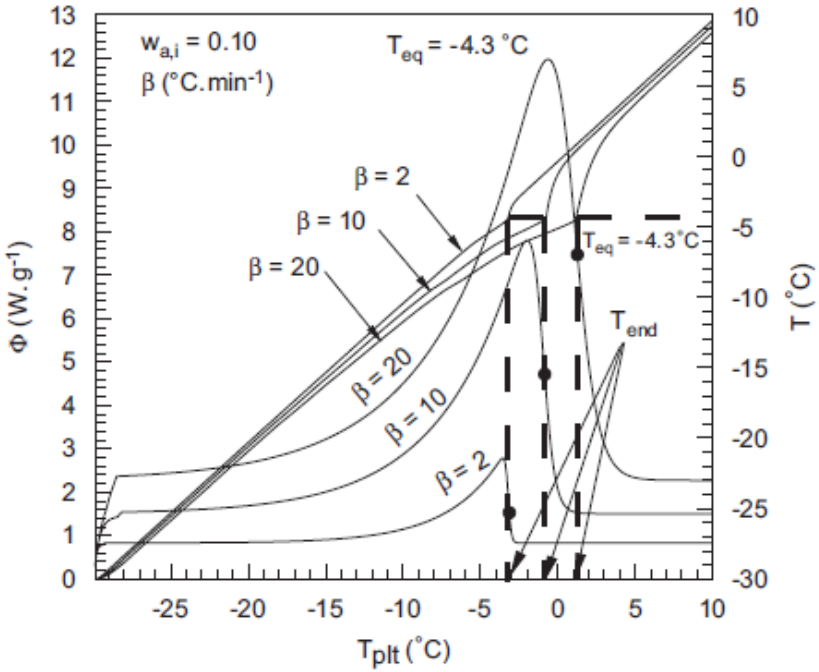


Fig. 8. Point of the end melting on the thermograms for different β.

Kousksou, T., Jamil, A., Zeraouli, Y., & Dumas, J. P. (2007). Equilibrium liquidus temperatures of binary mixtures from differential scanning calorimetry. *Chemical Engineering Science*, *62*(23), 6516-6523.

Равновесный ликвидус из ДСК эксп.

Совпадает с перегибом

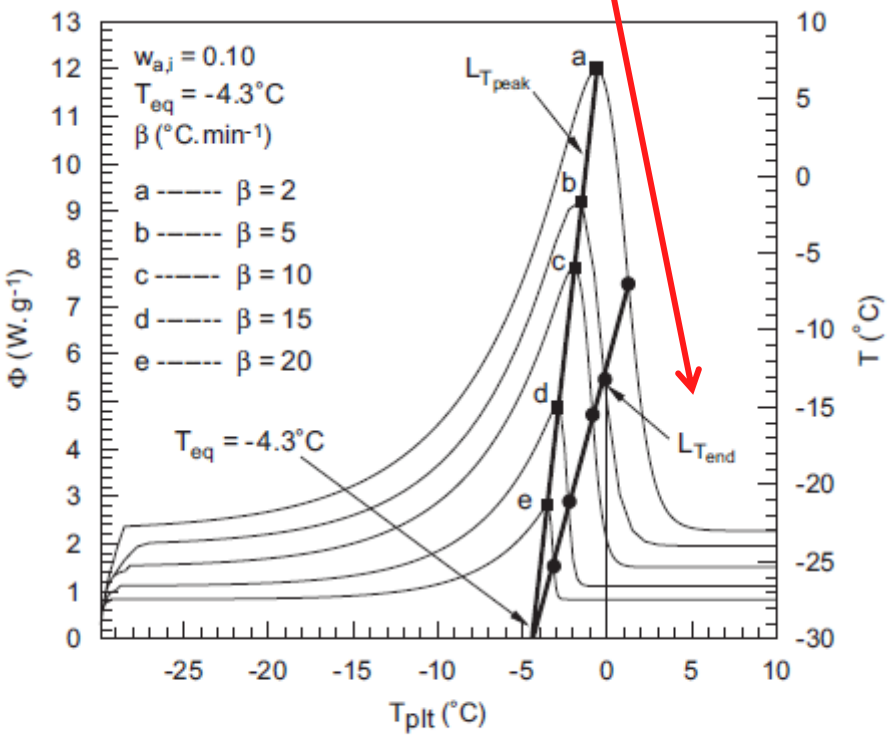


Fig. 9. Determination of equilibrium temperature for $W_{a,i} = 0.1$.

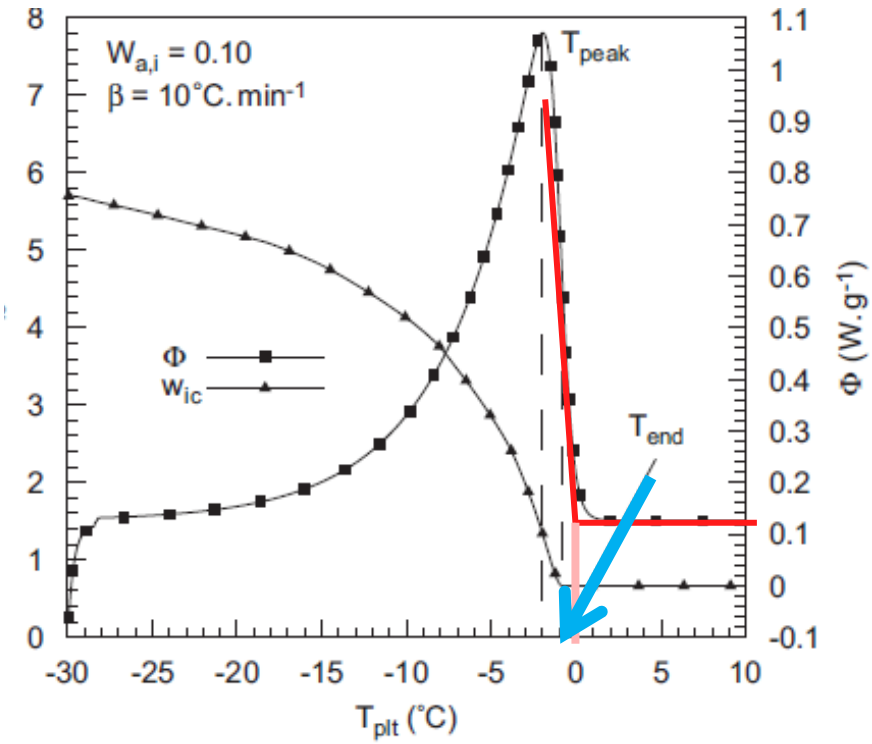


Fig. 5. Total ice mass fraction inside the sample versus T_{plt}.

Kousksou, T., Jamil, A., Zeraouli, Y., & Dumas, J. P. (2007). Equilibrium liquidus temperatures of binary mixtures from differential scanning calorimetry. *Chemical Engineering Science*, *62*(23), 6516-6523.

Ликвидус вне эвтектики

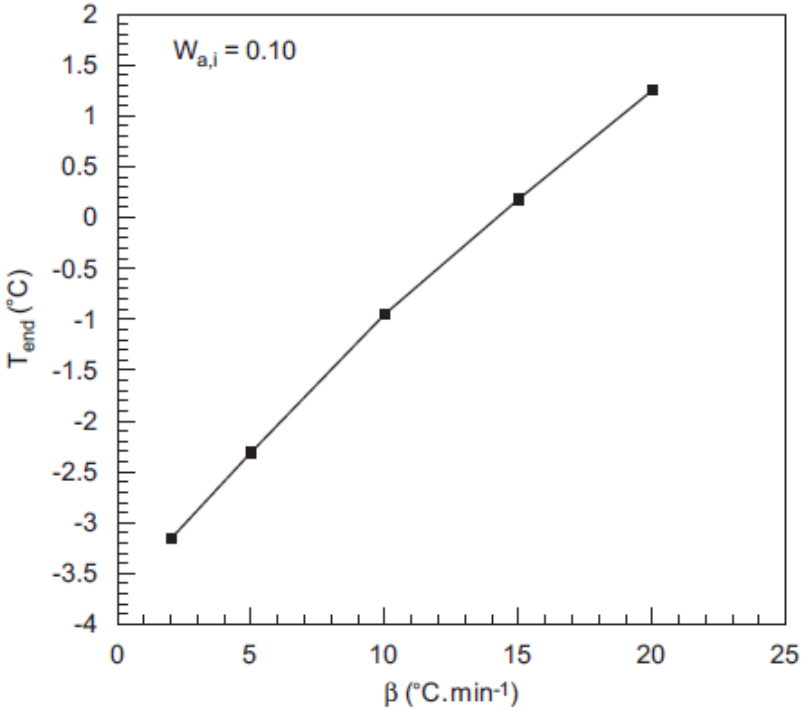


Fig. 6. T_{end} for different heating rate.

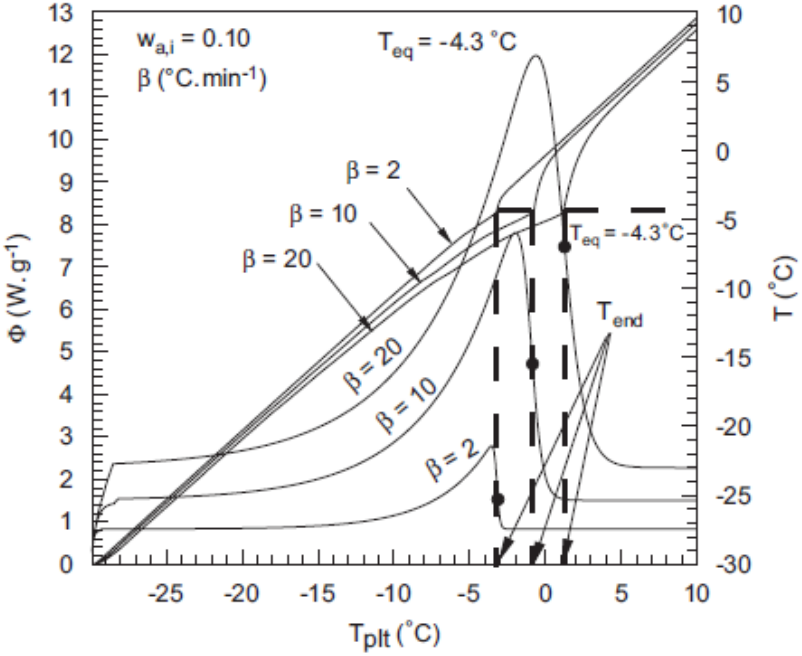


Fig. 8. Point of the end melting on the thermograms for different β.

Kousksou, T., Jamil, A., Zeraouli, Y., & Dumas, J. P. (2007). Equilibrium liquidus temperatures of binary mixtures from differential scanning calorimetry. *Chemical Engineering Science*, *62*(23), 6516-6523.

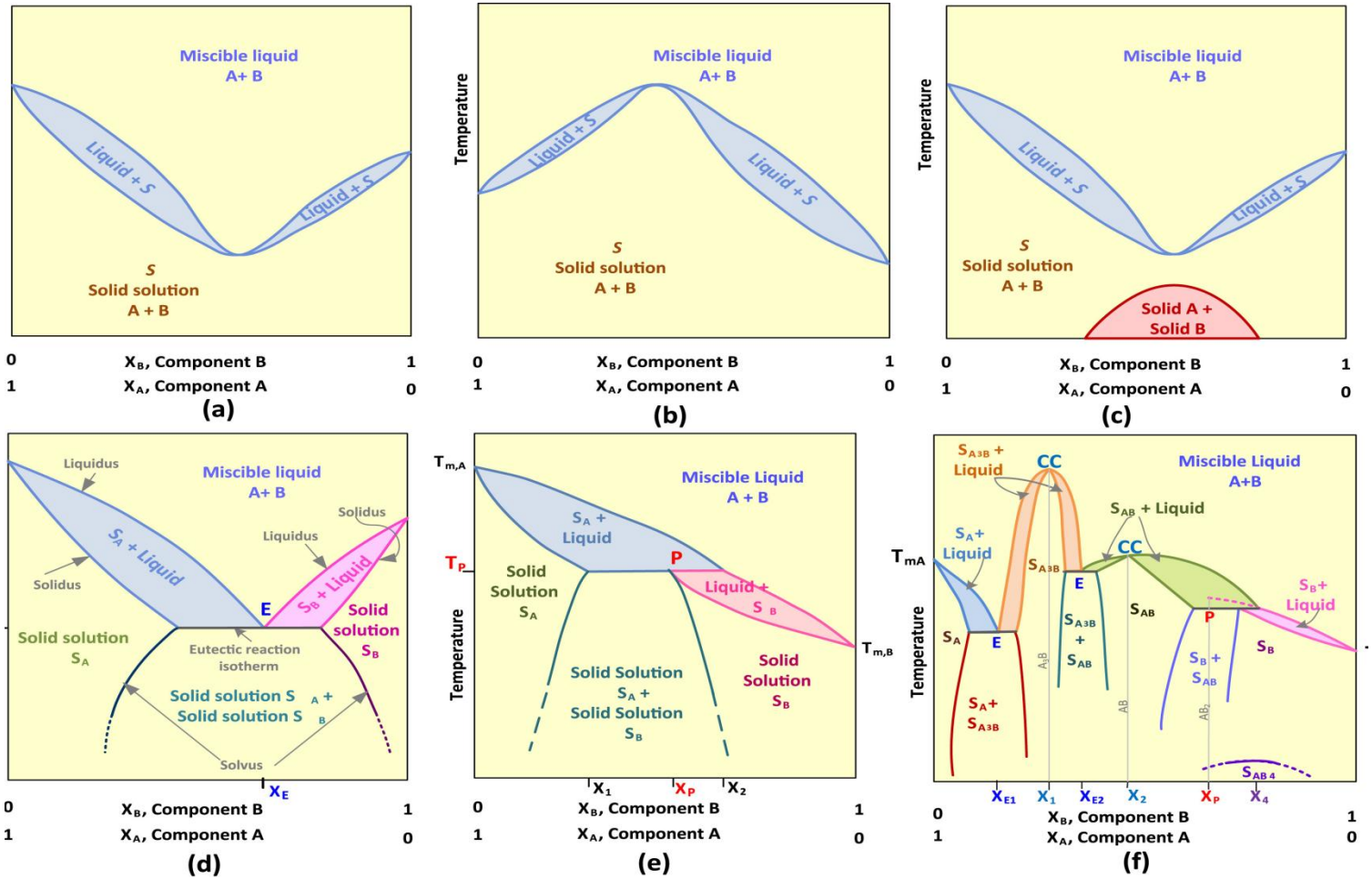


Рис. из 10.1016/j.rser.2017.01.108

Диаграммы с ***твёрдыми растворами.***

Как правильно определять фазовые границы?

Неполная растворимость

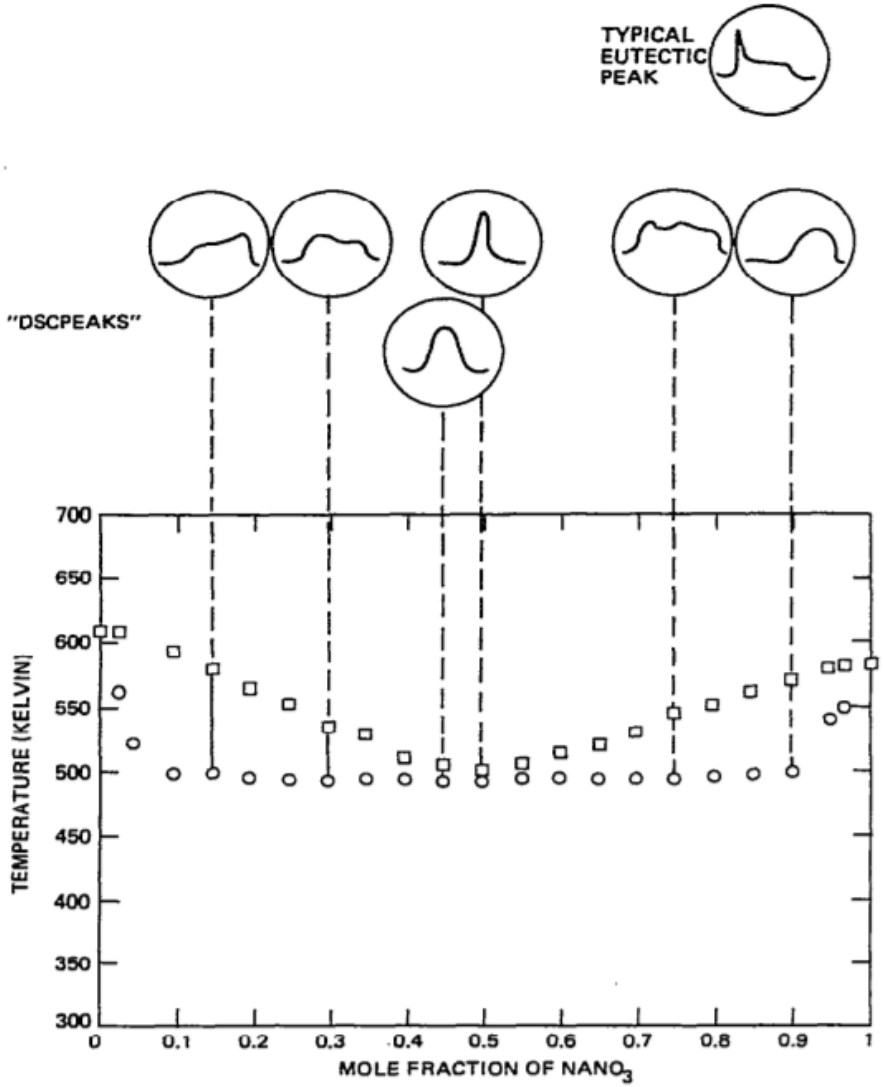


Fig. 2. DSC peaks for different $NaNO_3$—KNO_3 compositions shown with the solidus and liquidus data.

- Солидус – onset,
- Ликвидус – end
- Разные скорости сканирования, больше 10 К/мин – нет сходимости

Kramer, C. M., & Wilson, C. J. (1980). The phase diagram of NaNO3—KNO3. *Thermochimica Acta*, *42*(3), 253-264.

Неполная растворимость

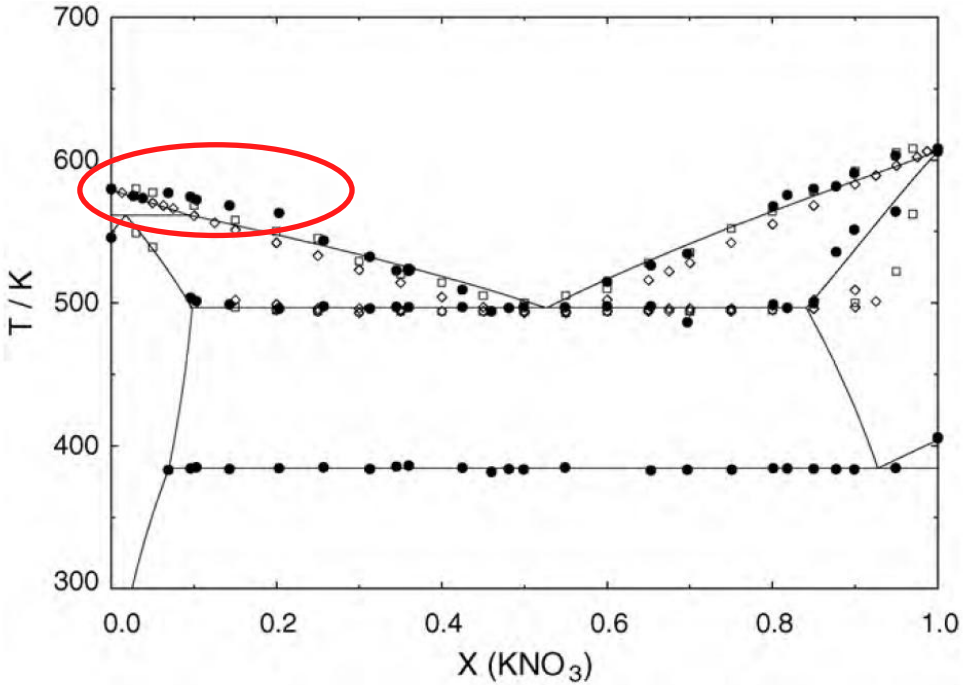


Fig. 5. The optimized $NaNO_3$–KNO_3 phase diagram, (●) DSC data obtained in this study, (□) DSC data obtained by Kramer and Wilson [28], and (◊) DSC data obtained by Greis et al. [31].

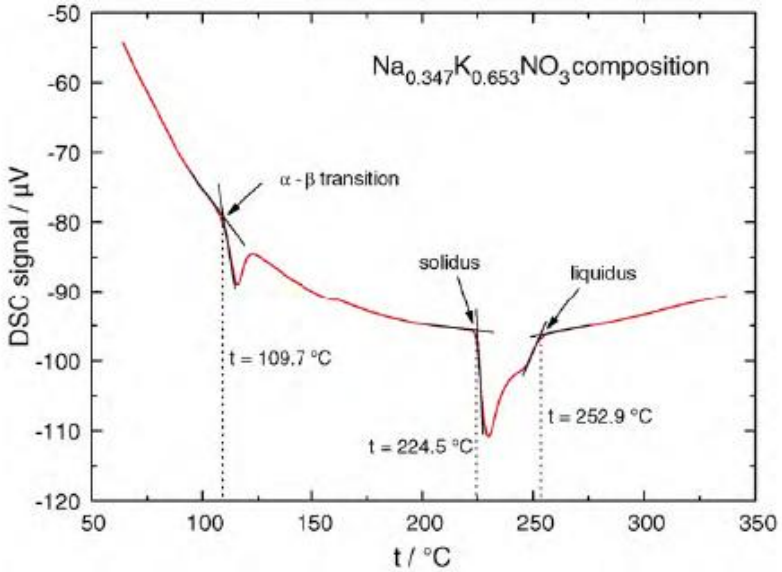


Fig. 4. DSC analysis of the measurement of the $Na_{0.347}K_{0.653}NO_3$ composition.

Снимали на охлаждении, «корректируя» переохлаждение по выборочным циклам на нагреве, прибавляя 3 К

Beneš, O., Konings, R. J. M., Wurzer, S., Sierig, M., & Dockendorf, A. (2010). A DSC study of the NaNO3–KNO3 system using an innovative encapsulation technique. *Thermochimica acta*, *509*(1-2), 62-66.

Полная растворимость + расслаивание

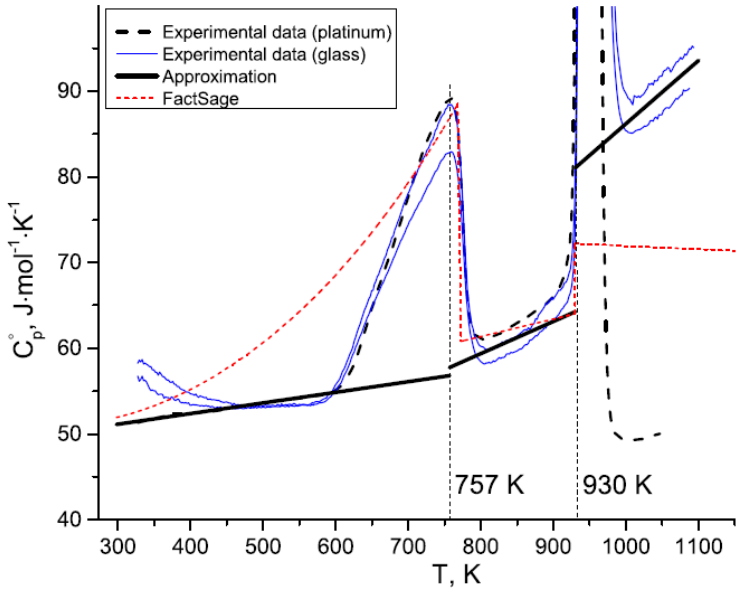


Fig. 2. Comparison of the heat capacity of solid and liquid phases of the 50 mol% NaCl – 50% KCl mixture determined in a platinum pan and a glass ampoule.

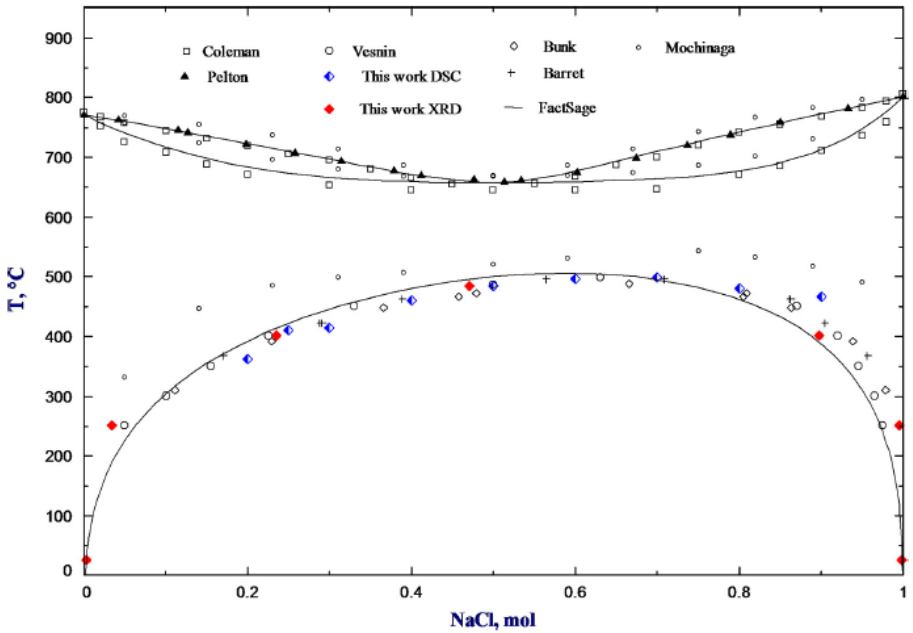


Fig. 8. Phase diagram of the the NaCl–KCl system: black lines – calculation by FactSage [11,25], Coleman – [10], Pelton – [11], Vesnin – [18], Bunk – [17], Barret – [16], Mochinaga – [12] and experimental data obtained in this work by DSC and XRD.

Sergeev, D., Kobertz, D., & Müller, M. (2015). Thermodynamics of the NaCl–KCl system. *Thermochimica acta*, *606*, 25-33.

Симуляция кривых ДСК (идеал. р-р)

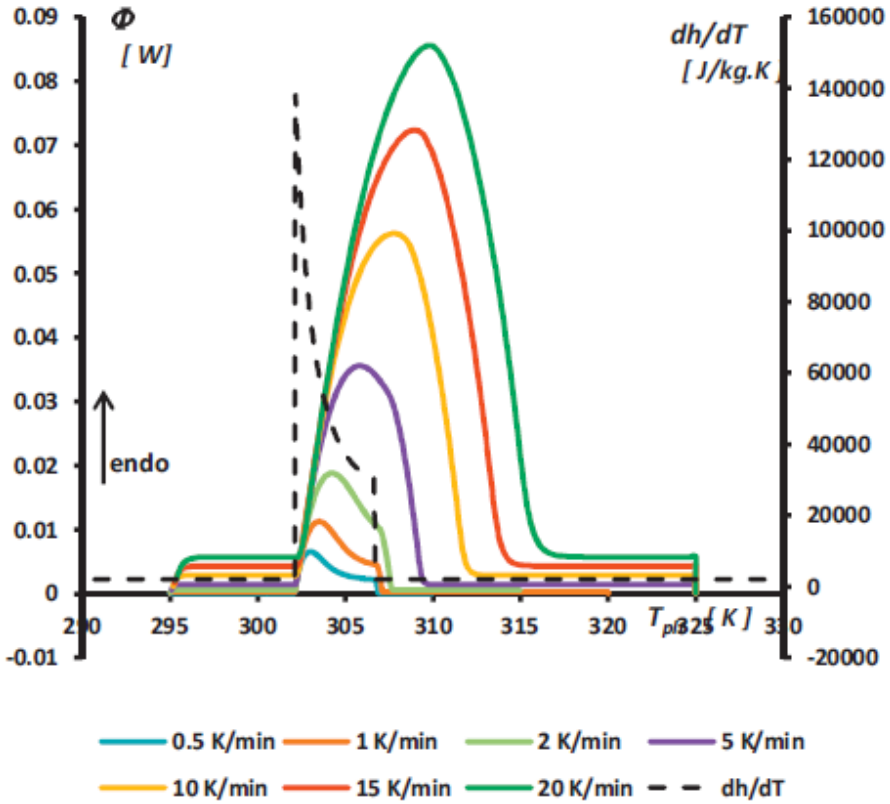
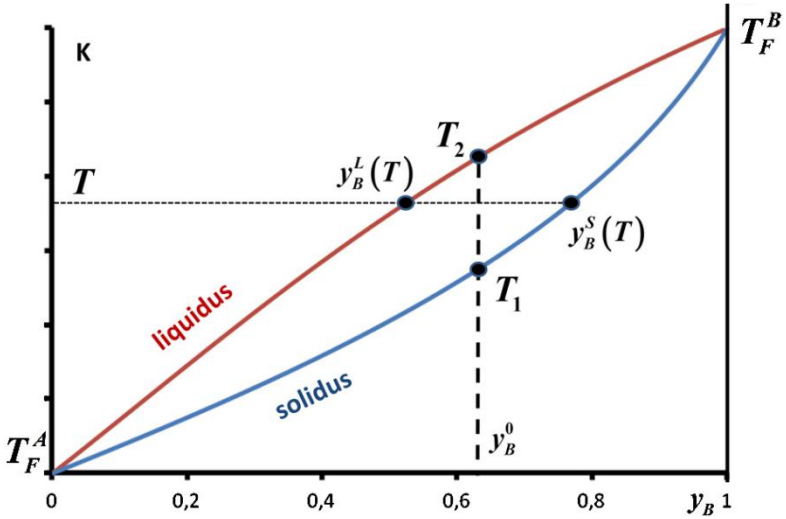


Fig. 6. Thermograms at different heating rates β and dh/dT for $y_B^0 = 0.2$.



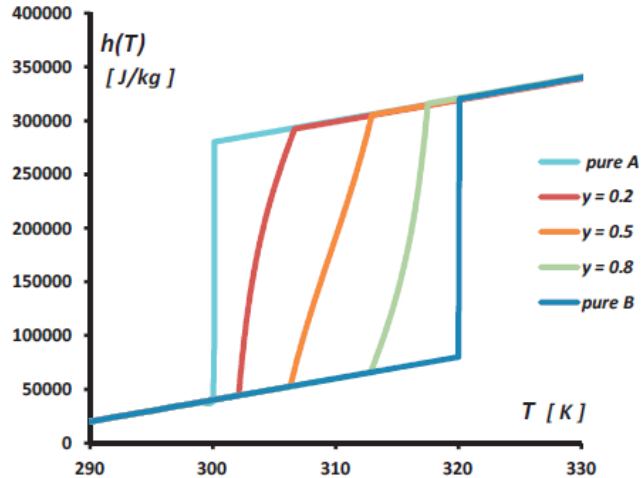


Fig. 5. Specific enthalpy at three concentrations and for the pure compounds.

Dumas, J. P., Gibout, S., Cézac, P., Franquet, E., & Haillot, D. (2013). Model for the DSC thermograms of the melting of ideal binary solutions. *Thermochimica acta*, *571*, 64-76.

Симуляция кривых ДСК (идеал. р-р)

$$c_P^{eq}[T_{plt}(t)] = \frac{\phi(t)}{m\beta}$$

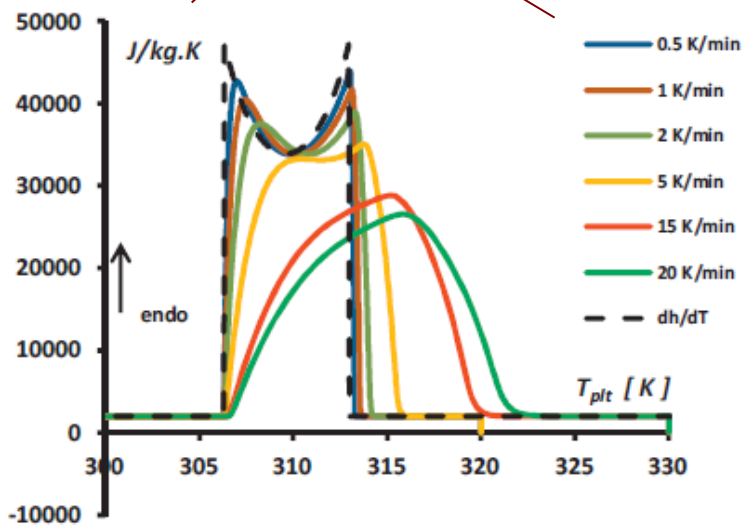


Fig. 10. Equivalent capacity at different heating rates β and comparison with dh/dT, for $y_B^0 = 0.5$.

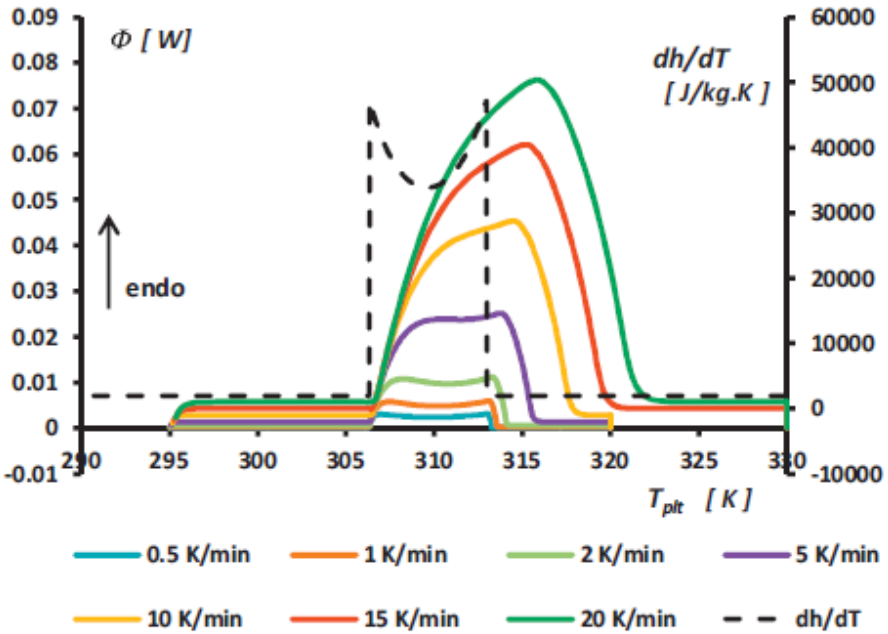


Fig. 7. Thermograms at different heating rates β and dh/dT for $y_B^0 = 0.5$.

Dumas, J. P., Gibout, S., Cézac, P., Franquet, E., & Haillot, D. (2013). Model for the DSC thermograms of the melting of ideal binary solutions. *Thermochimica acta*, *571*, 64-76.

Масса образца. Температура внутри

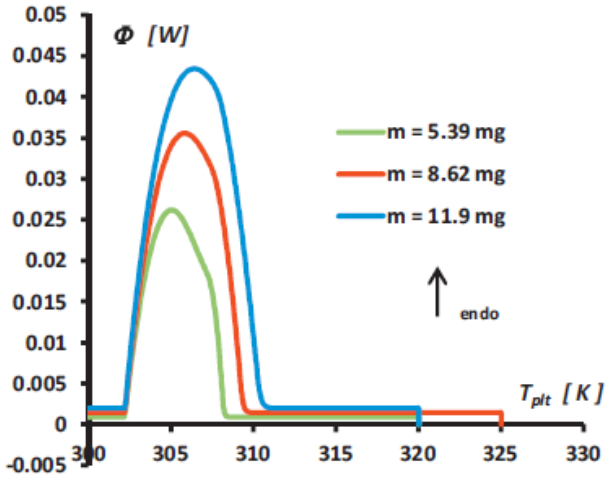


Fig. 12. Thermograms at 5 K min^{-1} for different masses of sample at $y_B^0 = 0.2$.

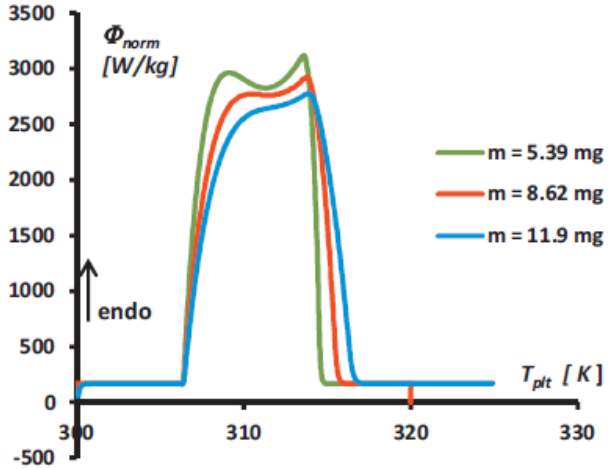


Fig. 16. Normalized thermograms at 5 K min^{-1} for different masses of sample at $y_B^0 = 0.5$.

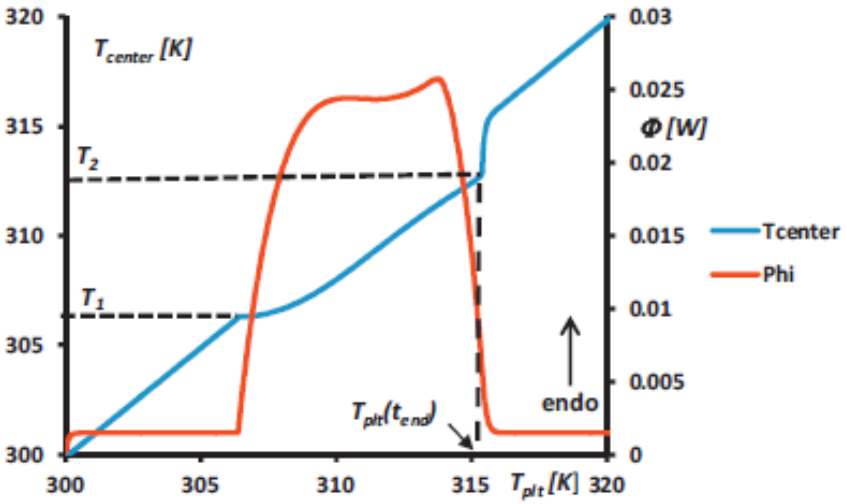


Fig. 21. Thermogram at 5 K min^{-1} and temperature of the center for $y_B^0 = 0.5$.

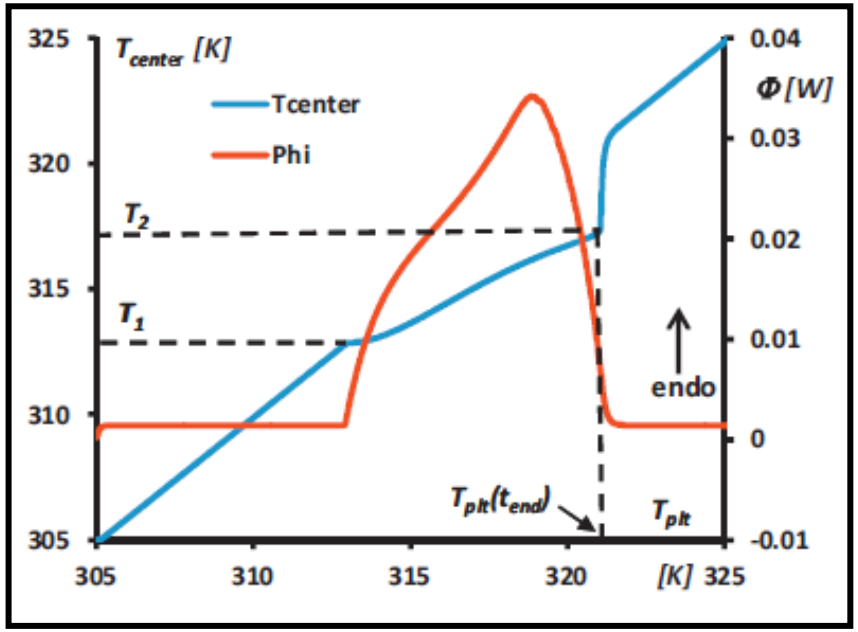
Рекомендация для солидуса: ONSET

Dumas, J. P., Gibout, S., Cézac, P., Franquet, E., & Haillot, D. (2013). Model for the DSC thermograms of the melting of ideal binary solutions. *Thermochimica acta*, *571*, 64-76.

Как определить Tl?

! Конечная температура – НЕ конец пика ДСК

Совпадает с перегибом, экстраполяция к β=0 К/мин ближе всего к Tl



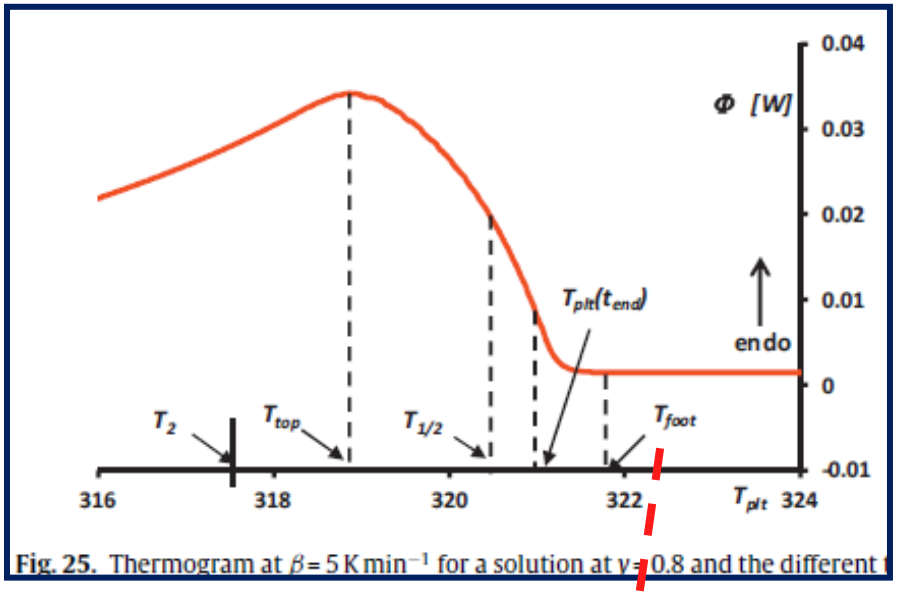
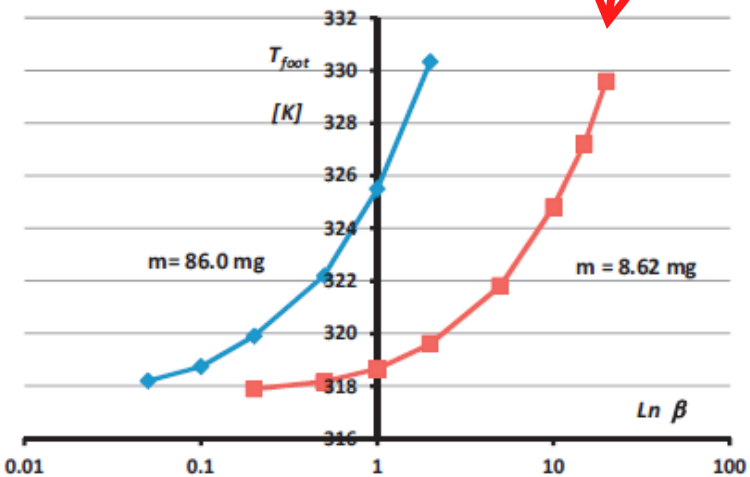


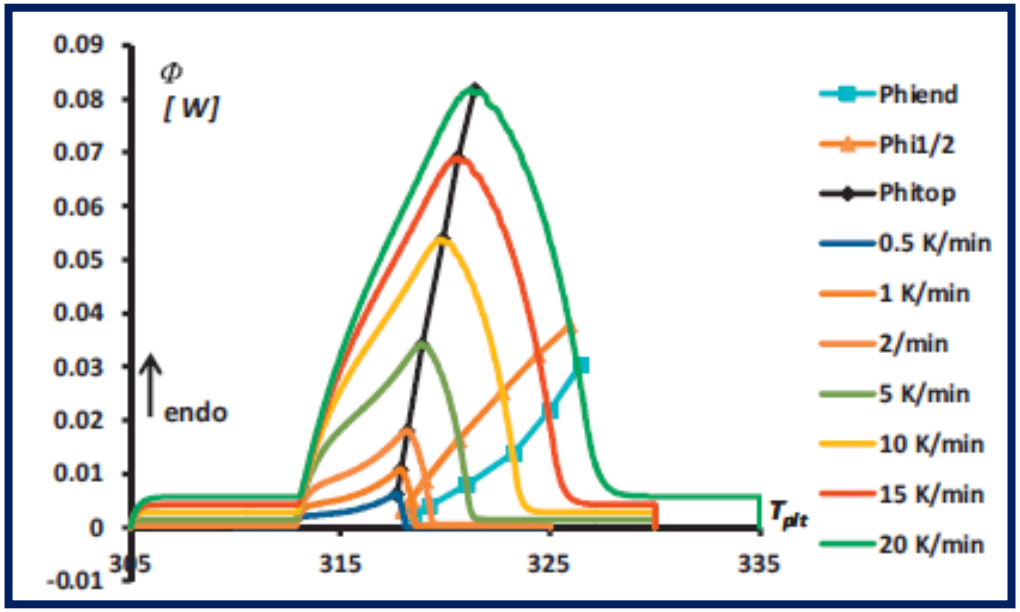
Fig. 25. Thermogram at $\beta = 5$ K min^{-1} for a solution at $y = 0.8$ and the different



Dumas, J. P., Gibout, S., Cézac, P., Franquet, E., & Haillot, D. (2013). Model for the DSC thermograms of the melting of ideal binary solutions. *Thermochimica acta*, *571*, 64-76.

Как определить Tl?

Соединить пики при разных β только при «острых» пиках и появлению «2» пика на средних скоростях



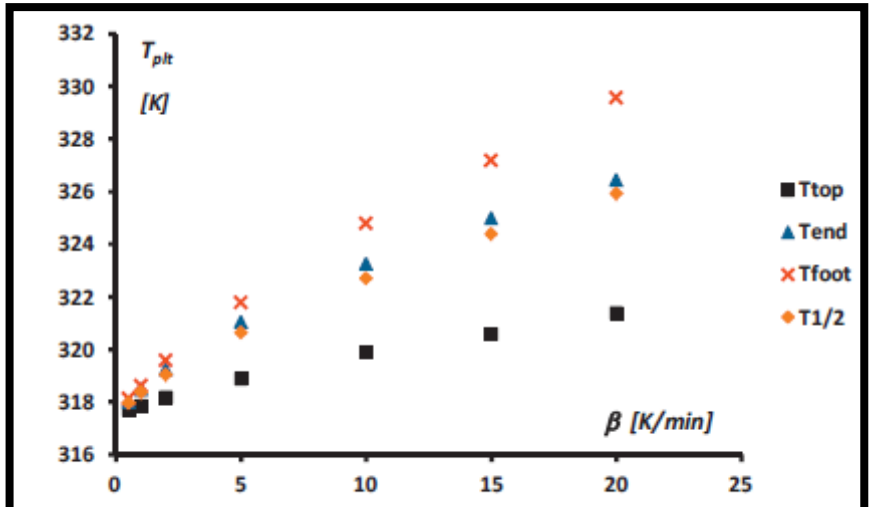


Fig. 27. T_{top}, $T_{plt}(t_{end})$, $T_{1/2}$ T_{foot} versus $\beta(y_B^0 = 0.8)$.

Полуэмпирическая корреляция:
при полувысоте T совпадает с исчезновением твердой фазы

Dumas, J. P., Gibout, S., Cézac, P., Franquet, E., & Haillot, D. (2013). Model for the DSC thermograms of the melting of ideal binary solutions. *Thermochimica acta*, *571*, 64-76.

Выводы

- Для определения **солидуса даже при наличии тв. растворов** «Начало» – лучший способ
- Для определения ликвидуса «Экстремум» - приемлемый способ без тв. растворов, лучше исп. $\beta \to 0$
- **Точка перегиба** при $\beta \to 0$ оказалась наиболее взаимосогласованной характеристикой экспериментально и теоретически для **ликвидуса, особенно если есть тв. растворы**