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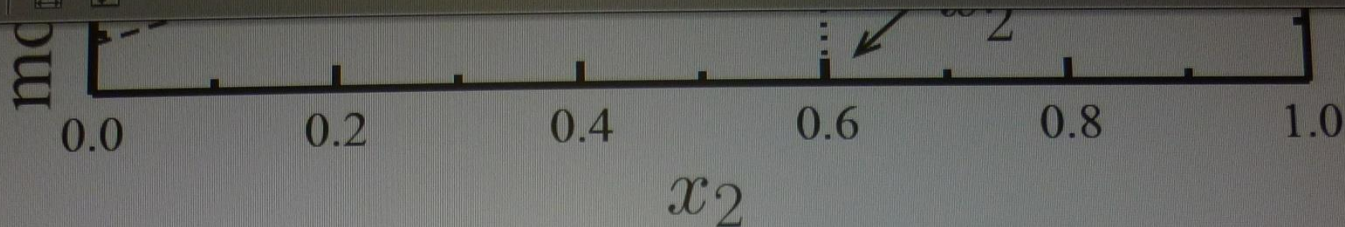


Figure 7.1: The molar Gibbs free energy G of a stable binary mixture as a function of the mole fraction of component 2 (solid line). The dashed line is the tangent line to G at the composition $x_2 = x_2^0$.

An ideal solution is never unstable and will always remain as a single phase mixture. To prove this, we need to demonstrate that $\partial^2 G^{\text{id}} / \partial x_2^2$ is always positive. For a binary mixture, the molar Gibbs free energy of an ideal solution is given by

$$\begin{aligned} G^{\text{id}} &= x_1 \mu_1^{\circ} + x_2 \mu_2^{\circ} + RT x_1 \ln x_1 + RT x_2 \ln x_2 \\ &= (1 - x_2) \mu_1^{\circ} + x_2 \mu_2^{\circ} + RT(1 - x_2) \ln(1 - x_2) + RT x_2 \ln x_2 \end{aligned} \quad (7.2)$$

Taking the derivative of this, we find

$$\begin{aligned} \text{I} \quad \frac{\partial G^{\text{id}}}{\partial x_2} &= \mu_2^{\circ} - \mu_1^{\circ} - RT \ln(1 - x_2) + RT \ln x_2 \\ \frac{\partial^2 G^{\text{id}}}{\partial x_2^2} &= \frac{RT}{1 - x_2} + \frac{RT}{x_2} \\ &= \frac{RT}{x_2(1 - x_2)} \end{aligned} \quad (7.3)$$

For all physical values of x_2 (i.e. $0 < x_2 < 1$), we see that $\partial^2 G^{\text{id}} / \partial x_2^2 > 0$. Therefore, the ideal

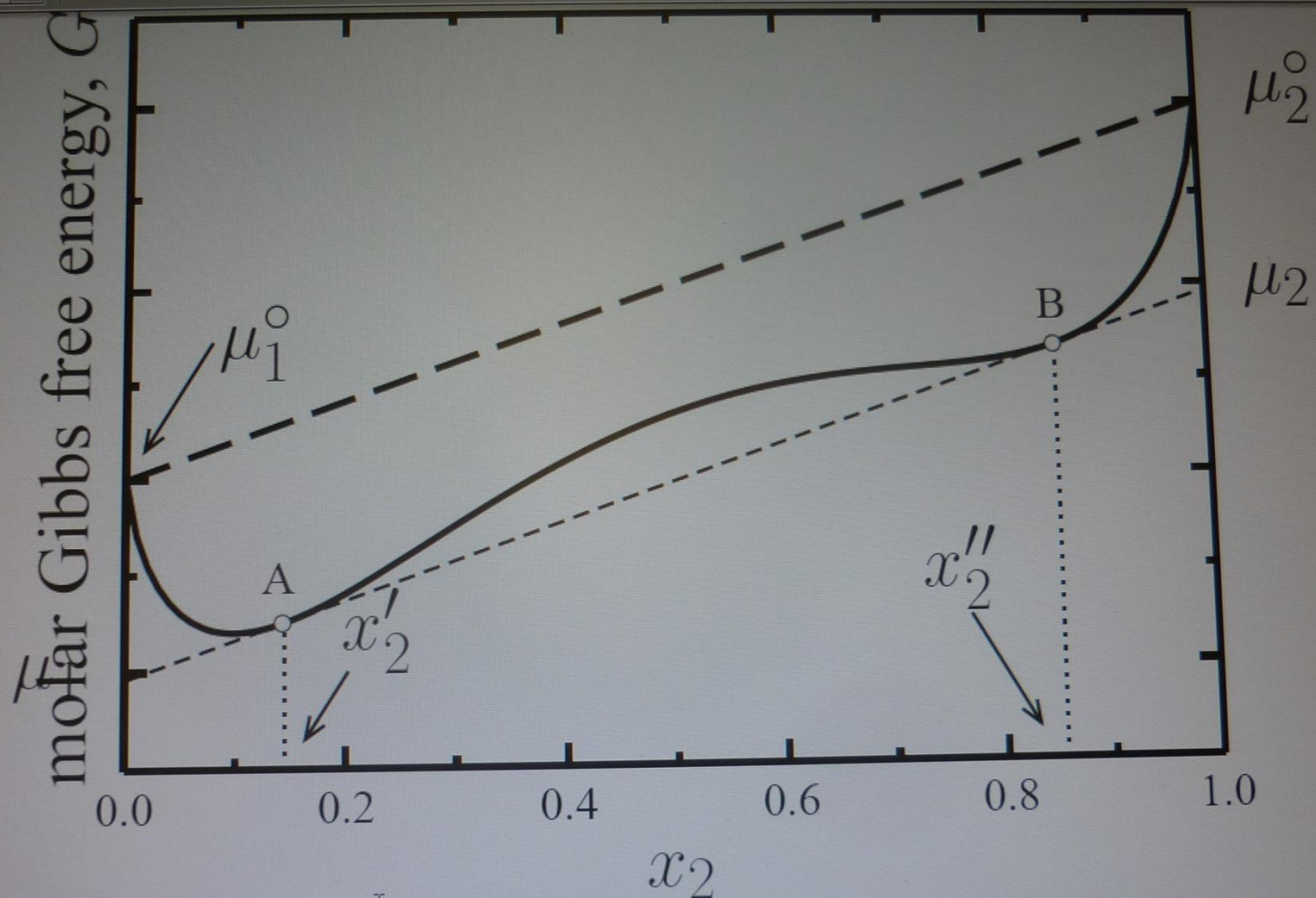


Figure 7.2: Variation of the molar Gibbs free energy G of a binary mixture as a function of the mole fraction of component 2 (solid line). The long-dashed line is the Gibbs free energy for a system of two unmixed pure compounds. The short-dashed line is the tangent line to G at the coexistence compositions $x_2 = x_2'$ and $x_2 = x_2''$.

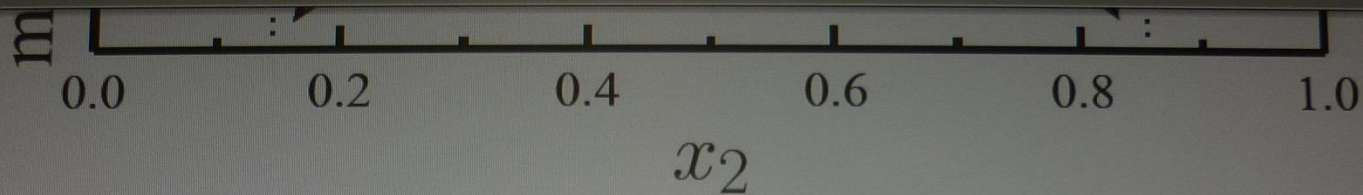


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To model a mixture that phase separates into two coexisting liquid phase, we need to add non-ideal terms (activity coefficients) to the ideal solution model. As an example of this, we examine the stability of the two-suffix Margules model, which has a molar Gibbs free energy of

$$\begin{aligned} G &= x_1\mu_1^\circ + x_2\mu_2^\circ + RTx_1 \ln x_1\gamma_1 + RTx_2 \ln x_2\gamma_2 \\ &= (1 - x_2)\mu_1^\circ + x_2\mu_2^\circ + RT(1 - x_2) \ln(1 - x_2) + RTx_2 \ln x_2 + RTA(1 - x_2)x_2 \end{aligned} \quad (7.4)$$

The derivatives of the molar Gibbs free energy are:

$$\begin{aligned} \frac{\partial G}{\partial x_2} &= -\mu_1^\circ + \mu_2^\circ - RT \ln(1 - x_2) + RT \ln x_2 + RTA(1 - 2x_2) \\ \frac{\partial^2 G}{\partial x_2^2} &= \frac{RT}{1 - x_2} + \frac{RT}{x_2} - 2RTA \\ &= \frac{RT}{x_2(1 - x_2)} - 2RTA \end{aligned} \quad (7.5)$$

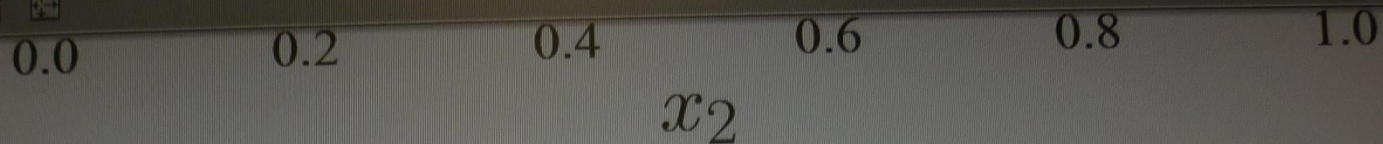


Figure 7.3: Stability diagram for the two-suffix Margules equation. The shaded region represents states where the Margules model predicts that the system is unstable.

7.2 Liquid-liquid equilibrium

When a liquid mixture becomes unstable, it separates into two coexisting liquid phases. We label one of the phases with a ' and the other phase with a ''. The criterion for phase equilibrium is

$$\begin{aligned}
 \mu'_\alpha &= \mu''_\alpha \\
 \mu^\circ_\alpha + RT \ln x'_\alpha \gamma'_\alpha &= \mu^\circ_\alpha + RT \ln x''_\alpha \gamma''_\alpha \\
 RT \ln x'_\alpha \gamma'_\alpha &= RT \ln x''_\alpha \gamma''_\alpha \\
 x'_\alpha \gamma'_\alpha &= x''_\alpha \gamma''_\alpha
 \end{aligned} \tag{7.7}$$

Given a model for the activity coefficients, Eq. (7.7) yields a set of constraints that can be solved for the compositions of each liquid phase.

Conversely, given the composition of the coexisting liquid phases, Eq. (7.7) can also be used to fit an activity coefficient model. For example, using the two-suffix Margules model for a binary mixture,

we can determine the parameter A

$$\begin{aligned}\ln \frac{\gamma_1'}{\gamma_1''} &= \ln \frac{x_1''}{x_1'} \\ Ax_2'^2 - Ax_2''^2 &= \ln \frac{x_1''}{x_1'} \\ A &= \frac{1}{x_2'^2 - x_2''^2} \ln \frac{x_1''}{x_1'}\end{aligned}\quad (7.8)$$



8.1 Introduction

At atmospheric pressure, water will freeze at 0°C . If a solute is added to water, then the mixture will freeze at a lower temperature. This is known as freezing point depression and occurs with any general mixture. Using a model for the activity coefficients, we can quantitatively predict the magnitude of this effect.

8.2 Phase behavior

To demonstrate the general freezing behavior of a binary mixture, we present the solid-liquid phase diagram for systems of ethanol and water at 1 atm in Fig. 8.1. The solid line with the filled symbols is the freezing curve of water in the mixture. Above the curve the solution is completely liquid; below the curve, it is a liquid mixture coexists with solid water (i.e., ice). At this pressure, pure water freezes at 273.15 K. As ethanol is added to the solution, the temperature at which ice begins to form gradually decreases.

The dotted line with the open symbols on the right side of the diagram is the freezing curve of ethanol in the mixture. As one passes downward through this curve, solid ethanol precipitates from the solution. Note that the temperature at which ethanol begins to freeze decreases as the amount of water in the solution increases. Therefore, we see that the addition of impurities decreases the freezing temperature of a substance. This phenomena is known as freezing point depression.

Finally, we note that below the dotted line in Fig. 8.1 the system exists as two coexisting solid phases: one consisting of pure ice, and the other composed of pure solid ethanol. The relative amounts of these two phases is given by the lever rule.

8.3 Conditions for equilibrium

In this section, we derive the equation that governs the shape of the freezing curve. Let's consider the freezing of a species in a general multicomponent mixture. We make the assumption that the solid phase consists of pure component α . At equilibrium, the chemical potential of the solid phase is the

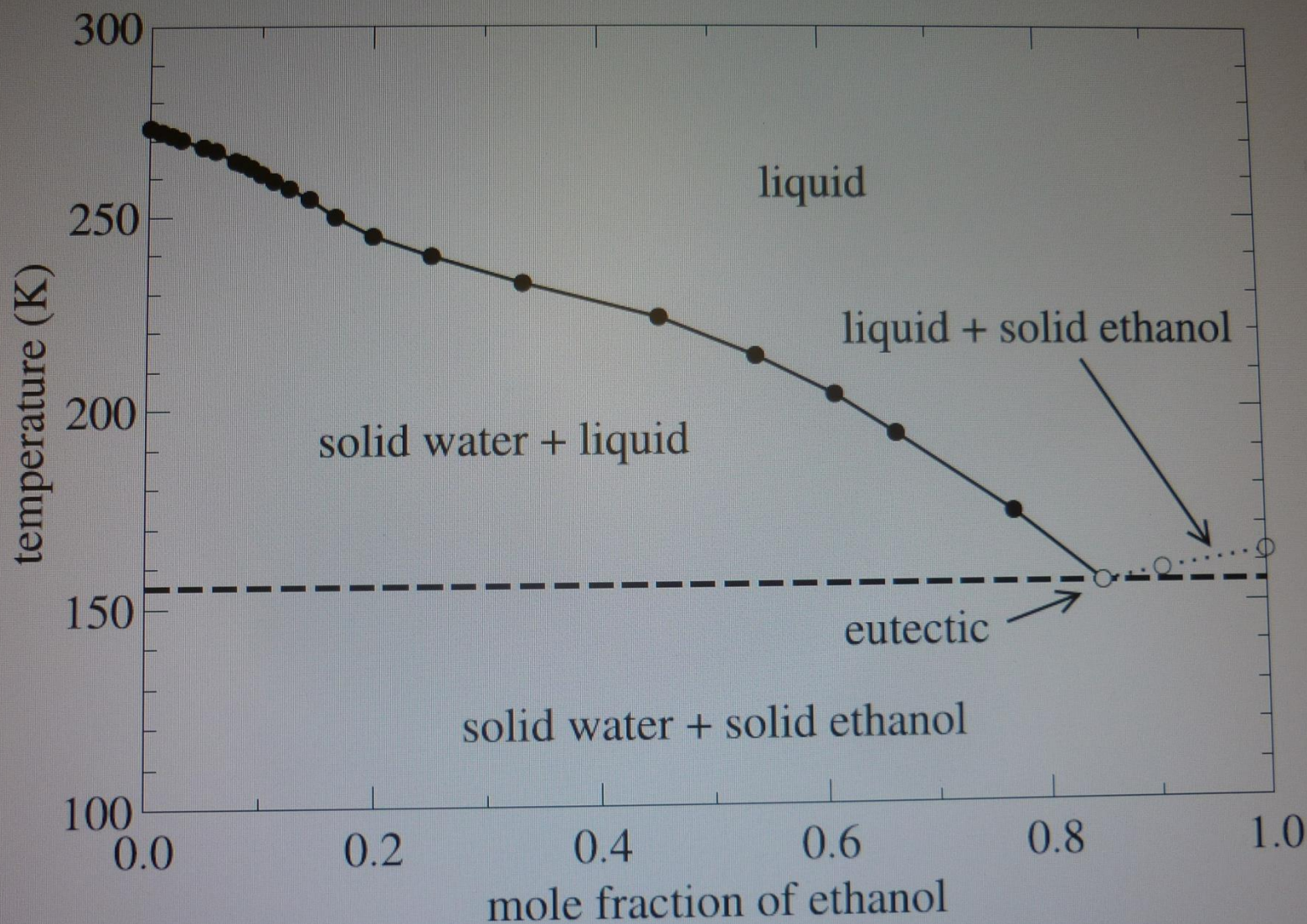


Figure 8.1: Solid-liquid phase diagram for mixtures of ethanol and water at 1 atm. Data taken from SU Pickering, *J. Chem. Soc.* **63**, 998 (1893).

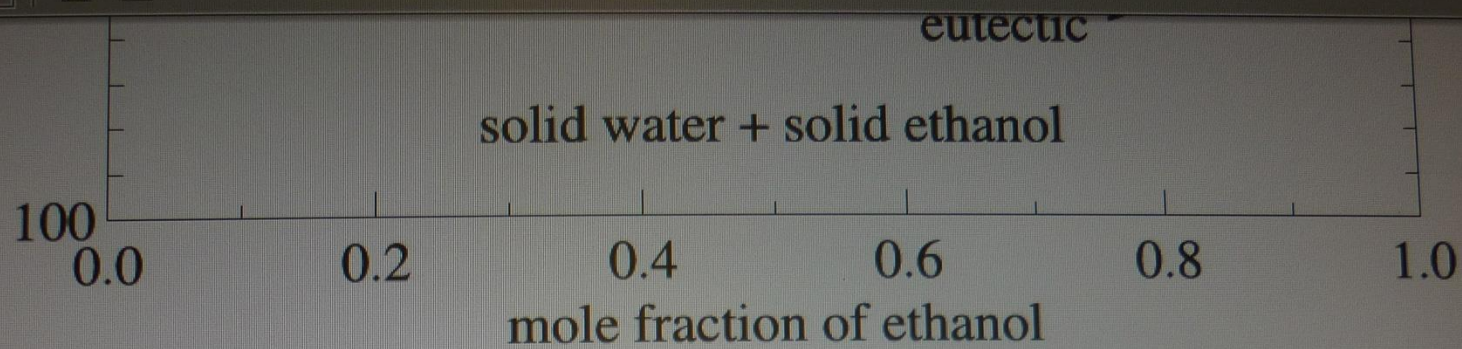


Figure 8.1: Solid-liquid phase diagram for mixtures of ethanol and water at 1 atm. Data taken from SU Pickering, *J. Chem. Soc.* **63**, 998 (1893).

same as that in the liquid phase:

$$\begin{aligned}\mu_{\alpha}^{(l)} &= \mu_{\alpha}^{(s)} \\ \mu_{\alpha}^{\circ, (l)}(T, p) + RT \ln x_{\alpha} \gamma_{\alpha} &= \mu_{\alpha}^{\circ, (s)}(T, p) \\ RT \ln x_{\alpha} \gamma_{\alpha} &= \mu_{\alpha}^{\circ, (s)}(T, p) - \mu_{\alpha}^{\circ, (l)}(T, p) \\ \ln x_{\alpha} \gamma_{\alpha} &= \frac{\Delta G_{\alpha}(T, p)}{RT}\end{aligned}\tag{8.1}$$

where ΔG_{α} is the difference in the chemical potentials of the solid and liquid phases (i.e., $\Delta G_{\alpha}(T, p) = \mu_{\alpha}^{\circ, (s)}(T, p) - \mu_{\alpha}^{\circ, (l)}(T, p)$). If we knew the composition of the mixture (i.e., x_{α}), γ_{α} , and the function ΔG_{α} , then we could use Eq. (8.1) to predict the freezing temperature T of the mixture.

One method to approximate the function ΔG_{α} is by using a Taylor series expansion around the temperature T_m , the melting temperature of pure α at pressure p . This yields

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$$\Delta G_\alpha(T, p) \approx \Delta G_\alpha(T_m, p) + \frac{\partial \Delta G_\alpha(T_m, p)}{\partial T} (T - T_m) + \dots \quad (8.2)$$

At the melting temperature T_m , the molar Gibbs free energy of the pure solid phase is equal to the

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molar Gibbs free energy of the pure liquid phase. That is

$$\Delta G_\alpha(T_m, p) = 0 \quad (8.3)$$

Therefore, the first term of the Taylor series expansion in Eq. (8.2) vanishes.

From the fundamental equation of thermodynamics, we arrive at

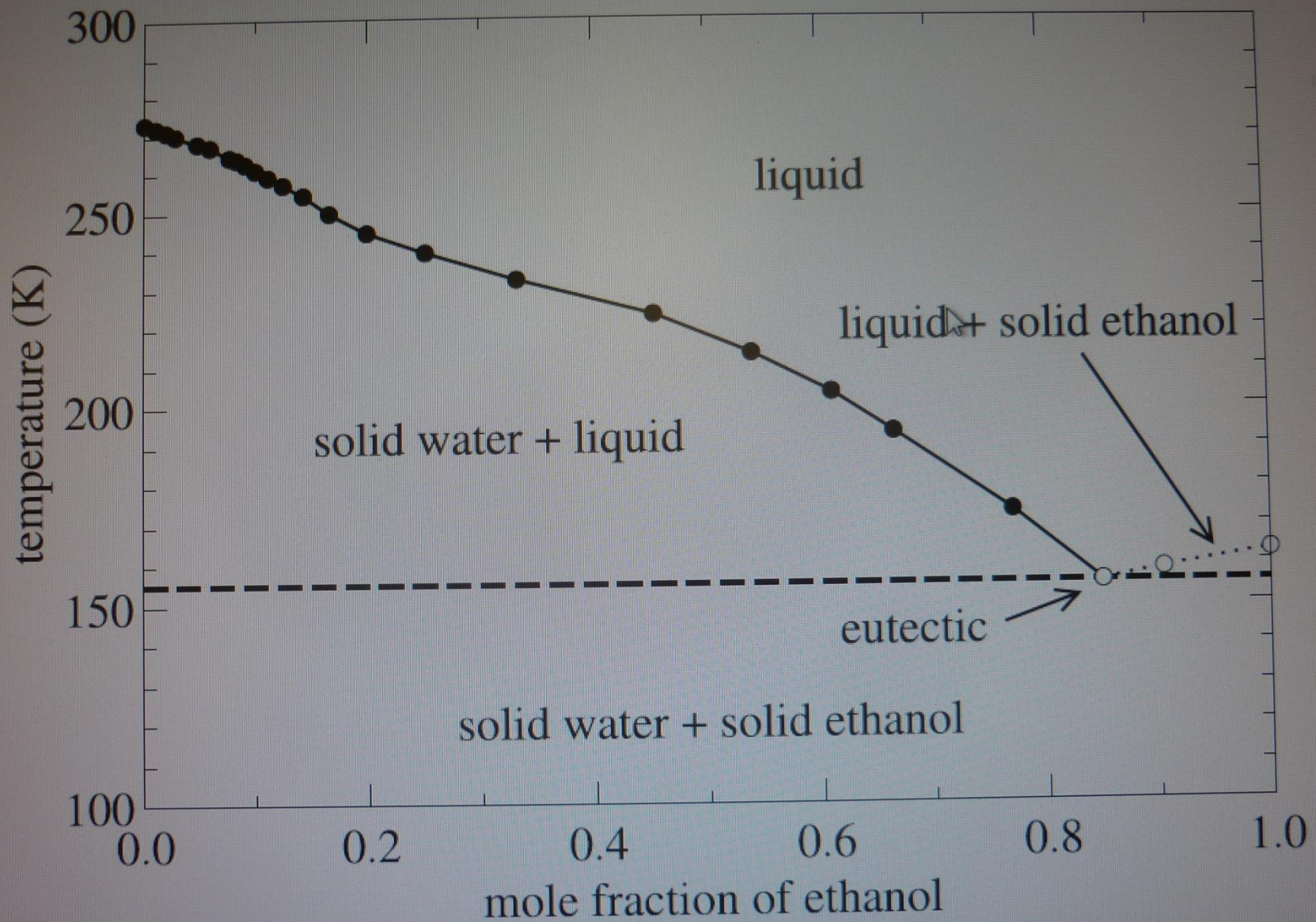


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same as that in the liquid phase:

$$\begin{aligned}
 \mu_{\alpha}^{(l)} &= \mu_{\alpha}^{(s)} \\
 \mu_{\alpha}^{\circ, (l)}(T, p) + RT \ln x_{\alpha} \gamma_{\alpha} &= \mu_{\alpha}^{\circ, (s)}(T, p) \\
 RT \ln x_{\alpha} \gamma_{\alpha} &= \mu_{\alpha}^{\circ, (s)}(T, p) - \mu_{\alpha}^{\circ, (l)}(T, p) \\
 \ln x_{\alpha} \gamma_{\alpha} &= \frac{\Delta G_{\alpha}(T, p)}{RT}
 \end{aligned} \tag{8.1}$$

where ΔG_{α} is the difference in the chemical potentials of the solid and liquid phases (i.e., $\Delta G_{\alpha}(T, p) = \mu_{\alpha}^{\circ, (s)}(T, p) - \mu_{\alpha}^{\circ, (l)}(T, p)$). If we knew the composition of the mixture (i.e., x_{α}), γ_{α} , and the function ΔG_{α} , then we could use Eq. (8.1) to predict the freezing temperature T of the mixture.

One method to approximate the function ΔG_{α} is by using a Taylor series expansion around the temperature T_m , the melting temperature of pure α at pressure p . This yields

$$\Delta G_{\alpha}(T, p) \approx \Delta G_{\alpha}(T_m, p) + \frac{\partial \Delta G_{\alpha}(T_m, p)}{\partial T} (T - T_m) + \dots \tag{8.2}$$

At the melting temperature T_m , the molar Gibbs free energy of the pure solid phase is equal to the

Finally, we find:

$$\begin{aligned}\ln x_{\alpha}\gamma_{\alpha} &= -\frac{\Delta H_{\alpha}(T_m, p)}{RTT_m}(T - T_m) \\ \ln x_{\alpha}\gamma_{\alpha} &= -\frac{\Delta H_{\alpha}(T_m, p)}{RT_m}\left(1 - \frac{T_m}{T}\right)\end{aligned}\quad (8.7)$$

This equation allows the prediction of the freezing curve of a mixture. It requires from knowledge of the freezing temperature and enthalpy of melting of the pure component α , as well as a model of the activity coefficients of the liquid mixture. In the absence of information for the activity coefficients, the ideal solution model can be used (i.e., $\gamma_{\alpha} = 1$); Eq. (8.7) then reduces to the van't Hoff equation.