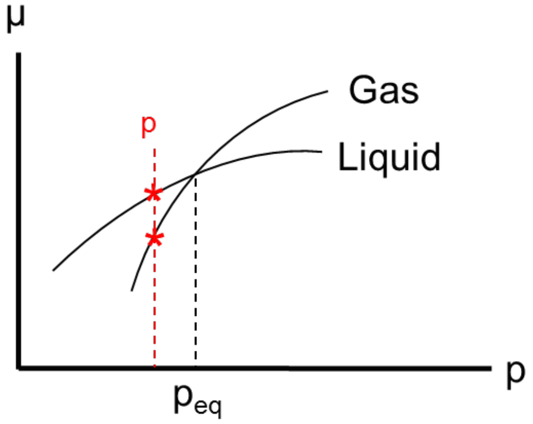
Homework 8 solutions

Exercise 1

Why do spray cans get cold? Explain why an aerosol spray can gets cold when you spray the contents.

The spray can is in liquid and gas equilibrium. It contains both liquid and gas. When we are spraying the can, some gas molecules leave the can. The pressure in the spray can then decrease. At this time, liquid and gas are no more in equilibrium. Liquid starts to boil and become gas. This can be explained by looking the μ, p diagram below. Gas is a more stable phase when the pressure drop below equilibrium pressure. Liquid turns into gas to rise the pressure and reach equilibrium.



In order for the component to transform from liquid to vapor, an amount of heat is required. During the transformation, the component absorbs heat from the can, causing it to get cold.

Exercise 2

In this exercise, we try to better understand the phase diagram of a typical material.

a) Consider the three coexistence lines of fusion, melting and vaporization. Based on your thermodynamic understanding, which of these is going to have the largest slope? Please explain your reasoning.

Based on the Clausius-Clapeyron equation, we know that $\left(\frac{dp}{dT}\right)_{eq} = \frac{L}{T\Delta v}$, where Δv is the difference in the molar volume between the two phases under consideration. We know that typically, the molar volume of a gas is about three orders of magnitudes larger than that of solids and liquids, while the molar volume of liquid and solids is on the same order of magnitude. Furthermore, the order of magnitude of the different latent heat does usually not change much.
Thus, we expect the slope of the fusion line to be the steepest since this is the line along which we divide by $\Delta v = v_l - v_s$ which is expected to be small.

b) Let us assume that we know the pressure p_{triple} and temperature T_{triple} at the triple point. For a given latent heat L_{vap} of vaporization (between the liquid and gas phase), calculate approximately the function $p_{vap}(T)$ that describes the pressure of Carbon dioxide along the vaporization line. Explain the used approximations.

The key idea here is to use the Clausius-Clapeyron equation $\left(\frac{dp}{dT}\right)_{eq} = \frac{L}{T\Delta v}$ and to integrate it.
Since the molar volume of gases is many orders of magnitude larger than that of the liquid, we simplify $\Delta v = v_g - v_l \approx v_g$.
Furthermore, we use the ideal gas law to approximate $v_g \approx \frac{RT}{p}$
As a third and final approximation, we will assume that the latent heat L_{lg} does not depend on the temperature.
Plugging this into the Clausius-Clapeyron equation and integration, we obtain

$$\left(\frac{dp}{dT}\right)_{eq} = \frac{L_{vap}}{T\Delta v} \approx \frac{L_{vap}p}{RT^2}$$
$$\frac{dp}{p} = \frac{L_{vap}}{R}\frac{dT}{T^2}$$
$$\ln\left(\frac{p}{p_0}\right) = \frac{L_{vap}}{R}\left(-\frac{1}{T} + \frac{1}{T_0}\right)$$
$$p_{vap} = p_0 e^{\frac{L_{vap}}{R}\left(-\frac{1}{T}+\frac{1}{T_0}\right)}$$

c) For a given latent heat L_{subl} of sublimation, calculate approximately the function $p_{subl}(T)$ that describes the pressure along the sublimation line.

Since the molar volume of a solid is on the same order of magnitude as a liquid, we can use the same approximations and directly obtain
$$p_{subl} = p_0 e^{\frac{L_{subl}}{R}\left(-\frac{1}{T}+\frac{1}{T_0}\right)}$$

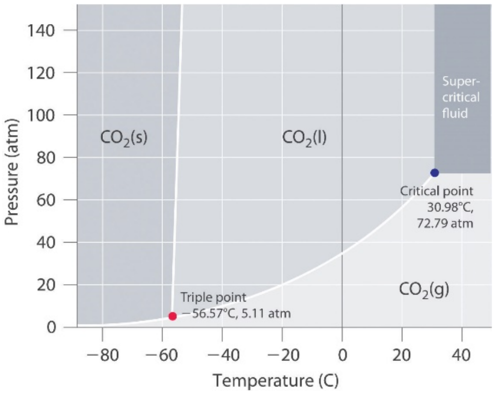
d) For a given latent heat L_{fus} of fusion, calculate approximately the function $p_{fus}(T)$ that describes the pressure along the fusion line. Explain the used approximations.

In this case, we are no longer allowed to simplify the volume difference $\Delta v = v_s - v_l$ since the two terms are on the same order of magnitude. Instead, we shall assume that the difference remains constant and does not depend on the temperature along the fusion line. As before, we assume that the latent heat is independent of the temperature as well. Then, we obtain

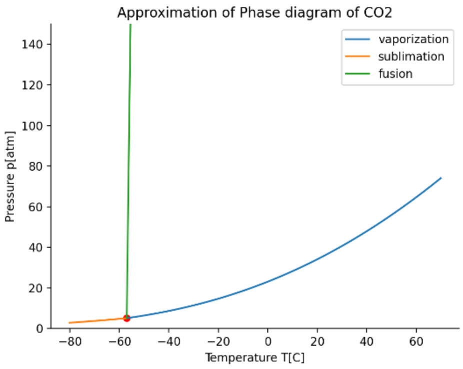
$$\left(\frac{dp}{dT}\right)_{eq} = \frac{L_{fus}}{T\Delta v}$$
$$dp = \frac{L_{fus}}{\Delta v}\frac{dT}{T}$$
$$p - p_0 = \frac{L_{fus}}{\Delta v}\ln\left(\frac{T}{T_0}\right)$$

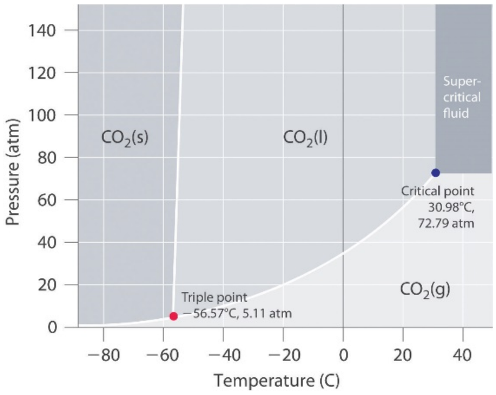
$$p = p_0 + \frac{L_{fus}}{\Delta v} \ln\left(\frac{T}{T_0}\right)$$

e) For Carbon dioxide, the explicit values are given by:
Triple point at p_{triple} =5.1atm and temperature $T_{triple} = -57$°C.
Molar volumes: v_s =28ml/mol, v_l =40ml/mol, v_g =22l/mol
Latent heats: $L_{subl} = 8.8$kJ/mol, $L_{vap} = 13$kJ/mol, $L_{fus} = 25$kJ/mol
Plot the complete phase diagram of the system and compare it to the experimental phase diagram shown below:



The important thing to notice is that all three curves computed in the previous exercises meet at the triple point. Thus, we can use the values of the triple point for T_0 and p_0 in the formulae above, as well as the correct latent heats for the respective curves. This provides us with the following phase diagram:





Qualitatively, our phase diagram looks pretty good compared to the experimental one. An obvious “mistake” is that our approach does not know about the existence of the critical point which was to be expected since we didn’t put any information about it in the calculations.
Beyond this, we can see that while not perfect, our oversimplified models seem to capture many essential features of the correct phase diagram. Clearly, if we would use the more exact latent heats and volume differences that depend on the temperature, we would get even better results.

f) Explain why or why not using the ideal gas approximation for the calculations done in this exercise are justified from a conceptual point of view.

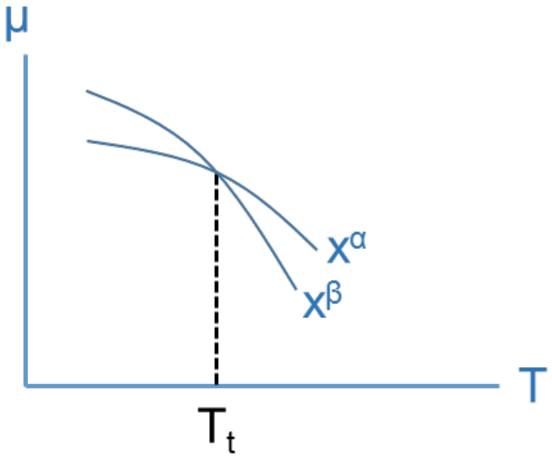
In the ideal gas law, we are completely neglecting the interactions between the particles. On the other hand, if we have a phase transition to the liquid or solid phase from the gas phase, it means that the interactions between the particles has become so important that the behavior of the system becomes completely different. Thus, from a conceptual point of view, using the ideal gas law is completely unjustified.
In practice, the obtained predictions are still not too bad, at least after some rescaling, so it is a useful first approximation.

<u>Exercise 3</u>

An element x exists in nature in two different solid forms, x^α and x^β. The molar Gibbs energy of x^α and x^β at 298 K and atmospheric pressure (also called the standard Gibbs energy of formation) are 510 J/mol and 485 J/mol, respectively.

a) Plot the molar Gibbs free energy of x^α and x^β as a function of temperature at constant pressure. The standard molar entropies of x^α and x^β are 23.6 J/mol K and 34.8 J/mol K, respectively.

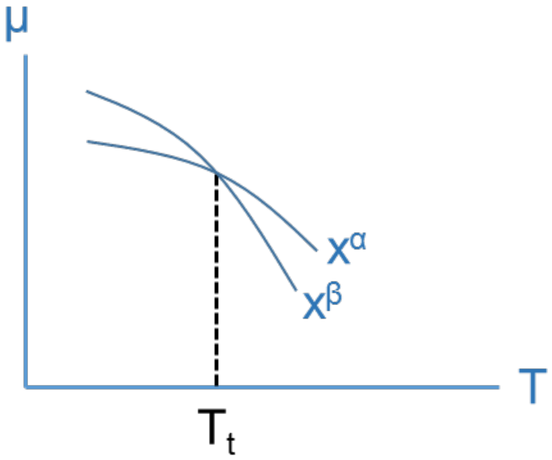
$$\left(\frac{\partial \mu}{\partial T}\right)_p = -s$$



Since the value of molar entropies $s^\beta > s^\alpha$, x^β has a more negative slope in (μ, T) diagram.

b) Under atmospheric pressure, does the increase in temperature make x^α more stable than x^β? If so, at what temperature will the transition occur? Which form of x is the more stable at 298 K?

No, the increase in the temperature won't make x^α more stable. Since x^β has a more negative slope, molar Gibbs free energy of x^β goes lower as the temperature increases. x_β will be more stable when the temperature increases.



Assume that molar entropies are not as a function of temperature

$$\left(\frac{\partial\mu}{\partial T}\right)_p = -s \qquad \mu = \mu^o - s(T - T_0)$$

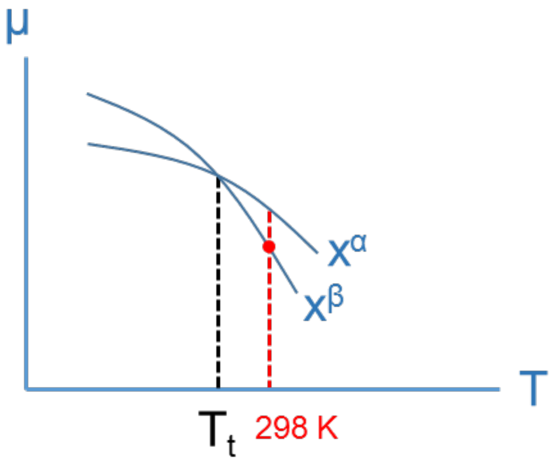
$$\Delta\mu = \mu^\beta - \mu^\alpha = 0 \quad \textit{when the transition occurs at } T_t$$

$$\mu^\beta = \mu^{o,\beta} - s(T_t - T_0) = 485 - 34.8(T_t - 298)$$

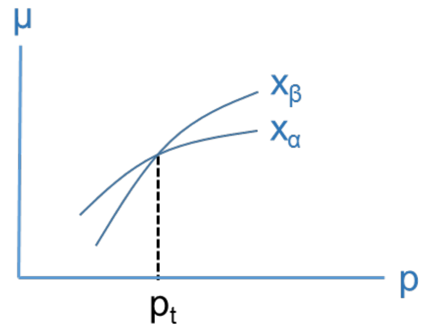
$$\mu^\alpha = \mu^{o,\alpha} - s(T_t - T_0) = 510 - 23.6(T_t - 298)$$

$$485 - 34.8(T_t - 298) = 510 - 23.6(T_t - 298) \qquad T_t = 295.76\ K$$

x_β is more stable since it has lower Gibbs free energy at 298 K.



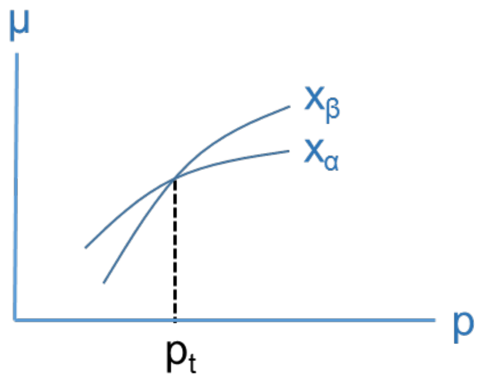
c) Plot the molar Gibbs free energy of x^α and x^β as a function of pressure at constant temperature. The molar volumes of x^α and x^β are 25 cm^3/mol and 30 cm^3/mol, respectively.



Since the value of molar volumes $v^\beta > v^\alpha$, x_β has a more positive slope in (μ, p) diagram.

d) Keeping the temperature constant at 298 K, does the increase in pressure make x^{α} more stable than x^{β}? If so, at what pressure will the transition occur?

Yes, the increase in the pressure makes x_{α} more stable. Since x_{α} has a less negative slope, molar Gibbs free energy of x_{α} goes lower when the pressure increases. x_{α} will be more stable when the pressure increases.



Consider the reaction: $x_{\alpha} \longrightarrow x_{\beta}$

$$\left(\frac{\partial \mu}{\partial p}\right)_T = v \qquad \mu = \mu^o + v(p - p_0)$$

$\Delta\mu = \mu^{\beta} - \mu^{\alpha} = 0$ when the transition occurs at p_t

$$\mu^{\beta} = \mu^{o,\beta} + v(p_t - p_0) = 485 + 30 * 10^{-6}(p_t - 101325)$$

$$\mu^{\alpha} = \mu^{o,\alpha} + v(p_t - p_0) = 510 + 25 * 10^{-6}(p_t - 101325)$$

$$485 + 30 * 10^{-6}(p_t - 101325) = 510 + 25 * 10^{-6}(p_t - 101325)$$

$$p_t = 5101325\ Pa = 51.01\ bar$$