

8.4: Coexistence Curves

A coexistence curve on a pressure–temperature phase diagram shows the conditions under which two phases can coexist in equilibrium, as explained in Sec. 8.2.2.

8.4.1 Chemical potential surfaces

From the relation $(\partial\mu/\partial T)_p = -S_m$, we see that at constant p the slope of μ versus T is negative since molar entropy is always positive. Furthermore, the magnitude of the slope increases on going from solid to liquid and from liquid to gas, because the molar entropies of sublimation and vaporization are positive. This difference in slope is illustrated by the curves for H_2O in Fig. 8.13(a). The triple-point pressure of H_2O is 0.0062 bar. At a pressure of 0.03 bar, greater than the triple-point pressure, the curves for solid and liquid intersect at a melting point (point A) and the curves for liquid and gas intersect at a boiling point (point B).

From $(\partial\mu/\partial p)_T = V_m$, we see that a pressure reduction at constant temperature lowers the chemical potential of a phase. The result of a pressure reduction from 0.03 bar to 0.003 bar (below the triple-point pressure of H_2O) is a downward shift of each of the curves of Fig. 8.13(a) by a distance proportional to the molar volume of the phase. The shifts of the solid and liquid curves are too small to see ($\Delta\mu$ is only $-0.002 \text{ kJ mol}^{-1}$). Because the gas has a large molar volume, the gas curve shifts substantially to a position where it intersects with the solid curve at a sublimation point (point C). At 0.003 bar, or any other pressure below the triple-point pressure, only a solid–gas equilibrium is possible for H_2O . The liquid phase is not stable at any pressure below the triple-point pressure, as shown by the pressure–temperature phase diagram of H_2O in Fig. 8.13(b).

8.4.2 The Clapeyron equation

If we start with two coexisting phases, α and β , of a pure substance and change the temperature of both phases equally without changing the pressure, the phases will no longer be in equilibrium, because their chemical potentials change unequally. In order for the phases to remain in equilibrium during the temperature change dT of both phases, there must be a certain simultaneous change dp in the pressure of both phases. The changes dT and dp must be such that the chemical potentials of both phases change equally so as to remain equal to one another: $d\mu^\alpha = d\mu^\beta$.

The infinitesimal change of μ in a phase is given by $d\mu = -S_m dT + V_m dp$ (Eq. 7.8.2). Thus, the two phases remain in equilibrium if dT and dp satisfy the relation

$$-S_m^\alpha dT + V_m^\alpha dp = -S_m^\beta dT + V_m^\beta dp \quad (8.4.2)$$

which we rearrange to

$$\frac{dp}{dT} = \frac{S_m^\beta - S_m^\alpha}{V_m^\beta - V_m^\alpha} \quad (8.4.3)$$

or

$$\frac{dp}{dT} = \frac{\Delta_{\text{trs}} S}{\Delta_{\text{trs}} V} \quad (8.4.4)$$

(pure substance)

Equation 8.4.4 is one form of the **Clapeyron equation**, which contains no approximations. We find an alternative form by substituting $\Delta_{\text{trs}} S = \Delta_{\text{trs}} H / T_{\text{trs}}$ (Eq. 8.3.5):

$$\frac{dp}{dT} = \frac{\Delta_{\text{trs}} H}{T \Delta_{\text{trs}} V} \quad (8.4.5)$$

(pure substance)

Equations 8.4.4 and 8.4.5 give the slope of the coexistence curve, dp/dT , as a function of quantities that can be measured. For the sublimation and vaporization processes, both $\Delta_{\text{trs}} H$ and $\Delta_{\text{trs}} V$ are positive. Therefore, according to Eq. 8.4.5, the solid–gas and liquid–gas coexistence curves have positive slopes. For the fusion process, however, $\Delta_{\text{fus}} H$ is positive, but $\Delta_{\text{fus}} V$ may be positive or negative depending on the substance, so that the slope of the solid–liquid coexistence curve may be either positive or negative. The absolute value of $\Delta_{\text{fus}} V$ is small, causing the solid–liquid coexistence curve to be relatively steep; see Fig. 8.13(b) for an example.

Most substances *expand* on melting, making the slope of the solid–liquid coexistence curve positive. This is true of carbon dioxide, although in Fig. 8.2(c) the curve is so steep that it is difficult to see the slope is positive. Exceptions

at ordinary pressures, substances that *contract* on melting, are H₂O, rubidium nitrate, and the elements antimony, bismuth, and gallium.

The phase diagram for H₂O in Fig. 8.4 clearly shows that the coexistence curve for ice I and liquid has a negative slope due to ordinary ice being less dense than liquid water. The high-pressure forms of ice are more dense than the liquid, causing the slopes of the other solid–liquid coexistence curves to be positive. The ice VII–ice VIII coexistence curve is vertical, because these two forms of ice have identical crystal structures, except for the orientations of the H₂O molecule; therefore, within experimental uncertainty, the two forms have equal molar volumes.

We may rearrange Eq. 8.4.5 to give the variation of p with T along the coexistence curve:

$$dp = \frac{\Delta_{\text{trs}}H}{\Delta_{\text{trs}}V} \cdot \frac{dT}{T} \quad (8.4.6)$$

Consider the transition from solid to liquid (fusion). Because of the fact that the cubic expansion coefficient and isothermal compressibility of a condensed phase are relatively small, $\Delta_{\text{fus}}V$ is approximately constant for small changes of T and p . If $\Delta_{\text{fus}}H$ is also practically constant, integration of Eq. 8.4.6 yields the relation

$$p_2 - p_1 \approx \frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V} \ln \frac{T_2}{T_1} \quad (8.4.7)$$

or

$$T_2 \approx T_1 \exp \left[\frac{\Delta_{\text{fus}}V(p_2 - p_1)}{\Delta_{\text{fus}}H} \right] \quad (8.4.8)$$

(pure substance)

from which we may estimate the dependence of the melting point on pressure.

8.4.3 The Clausius–Clapeyron equation

When the gas phase of a substance coexists in equilibrium with the liquid or solid phase, and provided T and p are not close to the critical point, the molar volume of the gas is much greater than that of the condensed phase. Thus, we may write for the processes of vaporization and sublimation

$$\Delta_{\text{vap}}V = V_{\text{m}}^{\text{g}} - V_{\text{m}}^{\text{l}} \approx V_{\text{m}}^{\text{g}} \quad \Delta_{\text{sub}}V = V_{\text{m}}^{\text{g}} - V_{\text{m}}^{\text{s}} \approx V_{\text{m}}^{\text{g}} \quad (8.4.9)$$

The further approximation that the gas behaves as an ideal gas, $V_{\text{m}}^{\text{g}} \approx RT/p$, then changes Eq. 8.4.5 to

$$\frac{dp}{dT} \approx \frac{p\Delta_{\text{trs}}H}{RT^2} \quad (8.4.10)$$

(pure substance,
vaporization or sublimation)

Equation 8.4.10 is the **Clausius–Clapeyron equation**. It gives an approximate expression for the slope of a liquid–gas or solid–gas coexistence curve. The expression is not valid for coexisting solid and liquid phases, or for coexisting liquid and gas phases close to the critical point.

At the temperature and pressure of the triple point, it is possible to carry out all three equilibrium phase transitions of fusion, vaporization, and sublimation. When fusion is followed by vaporization, the net change is sublimation. Therefore, the molar transition enthalpies at the triple point are related by

$$\Delta_{\text{fus}}H + \Delta_{\text{vap}}H = \Delta_{\text{sub}}H \quad (8.4.11)$$

Since all three of these transition enthalpies are positive, it follows that $\Delta_{\text{sub}}H$ is greater than $\Delta_{\text{vap}}H$ at the triple point. Therefore, according to Eq. 8.4.10, the slope of the solid–gas coexistence curve at the triple point is slightly greater than the slope of the liquid–gas coexistence curve.

We divide both sides of Eq. 8.4.10 by p° and rearrange to the form

$$\frac{d(p/p^\circ)}{p/p^\circ} \approx \frac{\Delta_{\text{trs}}H}{R} \cdot \frac{dT}{T^2} \quad (8.4.12)$$

Then, using the mathematical identities $d(p/p^\circ)/(p/p^\circ) = d\ln(p/p^\circ)$ and $dT/T^2 = -d(1/T)$, we can write Eq. 8.4.12 in three alternative forms:

$$\frac{d\ln(p/p^\circ)}{dT} \approx \frac{\Delta_{\text{trs}}H}{RT^2} \quad (8.4.13)$$

(pure substance,
vaporization or sublimation)

$$d\ln(p/p^\circ) \approx -\frac{\Delta_{\text{trs}}H}{R} d(1/T) \quad (8.4.14)$$

(pure substance,
vaporization or sublimation)

$$\frac{d\ln(p/p^\circ)}{d(1/T)} \approx -\frac{\Delta_{\text{trs}}H}{R} \quad (8.4.15)$$

(pure substance,
vaporization or sublimation)

Equation 8.4.15 shows that the curve of a plot of $\ln(p/p^\circ)$ versus $1/T$ (where p is the vapor pressure of a pure liquid or solid) has a slope at each temperature equal, usually to a high degree of accuracy, to $-\Delta_{\text{vap}}H/R$ or $-\Delta_{\text{sub}}H/R$ at that temperature. This kind of plot provides an alternative to calorimetry for evaluating molar enthalpies of vaporization and sublimation.

If we use the recommended standard pressure of 1 bar, the ratio p/p° appearing in these equations becomes p/bar . That is, p/p° is simply the numerical value of p when p is expressed in bars. For the purpose of using Eq. 8.4.15 to evaluate $\Delta_{\text{trs}}H$, we can replace p° by any convenient value. Thus, the curves of plots of $\ln(p/\text{bar})$ versus $1/T$, $\ln(p/\text{Pa})$ versus $1/T$, and $\ln(p/\text{Torr})$ versus $1/T$ using the same temperature and pressure data all have the same slope (but different intercepts) and yield the same value of $\Delta_{\text{trs}}H$.

If we assume $\Delta_{\text{vap}}H$ or $\Delta_{\text{sub}}H$ is essentially constant in a temperature range, we may integrate Eq. 8.4.14 from an initial to a final state along the coexistence curve to obtain

$$\ln \frac{p_2}{p_1} \approx -\frac{\Delta_{\text{trs}}H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (8.4.16)$$

(pure substance,
vaporization or sublimation)

Equation 8.4.16 allows us to estimate any one of the quantities p_1 , p_2 , T_1 , T_2 , or $\Delta_{\text{trs}}H$, given values of the other four.

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