

12.7: Phase Equilibria - Temperature Dependence of the Melting Point

We can also represent reversible changes by paths on contour maps. In Figure 5, a Gibbs free energy surface is represented as a contour map.

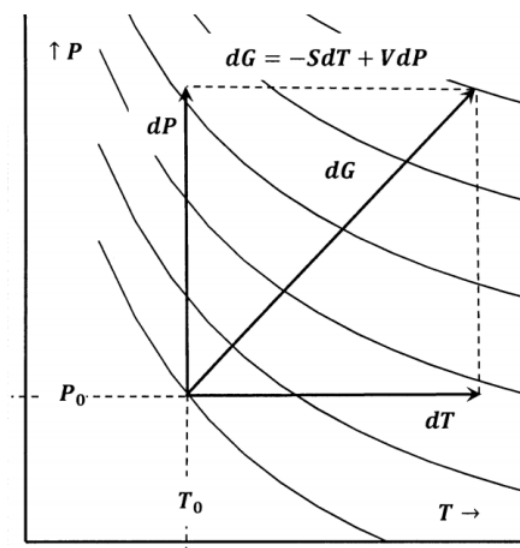


Figure 5. The path of a changing system depicted on a map of constant Gibbs free energy contours.

For small changes in T and P , we can evaluate

$$dG = G(P_0 + dP, T_0 + dT) - G(P_0, T_0)$$

from

$$dG = -S(P_0, T_0) dT + V(P_0, T_0) dP$$

For larger changes, we can integrate along the paths $P = P_0$ and $T = T_0 + \Delta T$ to find

$$\Delta G = \int_{T_0}^{T_0 + \Delta T} -S(P_0, T) dT + \int_{P_0}^{P_0 + \Delta P} V(P, T_0 + \Delta T) dP$$

The calculation of ΔS in [Section 12.5](#) could be similarly represented as a path in the temperature–pressure plane that connects two constant-entropy contours.

Analysis of solid–liquid equilibrium parallels that of liquid–vapor equilibrium. Let us again consider the equilibrium between ice and water. Given that ice and water are at equilibrium at a particular temperature and pressure, and supposing that we increase the pressure from this equilibrium value, how must the temperature change in order that the system remain at equilibrium? In [Section 6.6](#), we use Le Chatelier’s principle to answer this question qualitatively. Now, we find a quantitative answer by an argument that closely parallels that in [Section 12.7](#).

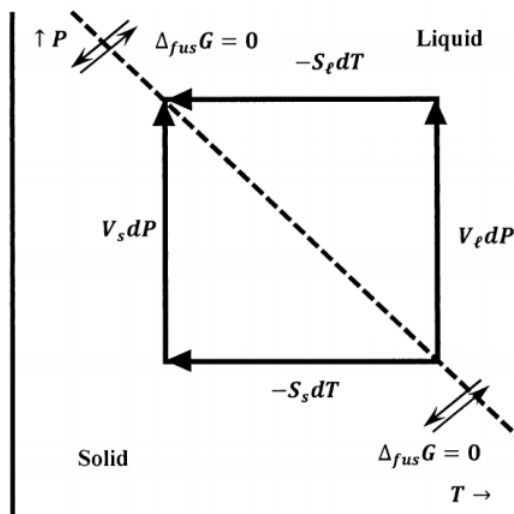


Figure 6. Gibbs free energy changes in a cycle connecting two solid-liquid equilibrium states.

Figure 6 depicts the line of pressures and temperatures along which ice and water are in equilibrium. We can view this as a contour map. In this case, the contours are sets of pressures and temperatures for which $\Delta_{fus}\bar{G}$ is constant. Only the contour for $\Delta_{fus}\bar{G} = 0$ is shown. The figure also depicts paths along which ice and water can individually be taken from their equilibrium state at P and T to their equilibrium state at $P + dP$ and $T + dT$. The Gibbs free energy change for the ice must equal that for water. Letting \bar{G}_ℓ , \bar{S}_ℓ , and \bar{V}_ℓ be the Gibbs free energy, the entropy, and the volume of one mole of water at temperature T and pressure P , the equation

$$d\bar{G}_\ell = \bar{V}_\ell dP - \bar{S}_\ell dT$$

specifies the change in the Gibbs free energy of one mole of water when the pressure changes P to $P + dP$ and the temperature changes from T to $T + dT$. Similarly, using the subscript “s” to denote ice, we have

$$d\bar{G}_s = \bar{V}_s dP - \bar{S}_s dT$$

Since these Gibbs free energy changes connect states of ice–water equilibrium, they must be equal, and we have

$$d\bar{G}_\ell - d\bar{G}_s = (\bar{V}_\ell - \bar{V}_s) dP - (\bar{S}_\ell - \bar{S}_s) dT = \Delta_{fus}\bar{V} dP - \Delta_{fus}\bar{S} dT = 0$$

where we introduce $\Delta_{fus}\bar{S}$ and $\Delta_{fus}\bar{V}$ to represent the entropy and volume changes that occur when one mole of ice melts reversibly at P and T . Rearranging gives

$$\frac{dP}{dT} = \frac{\Delta_{fus}\bar{S}}{\Delta_{fus}\bar{V}}$$

Since

$$\Delta_{fus}\bar{S} = \Delta_{fus}\bar{H}/T,$$

the Clapeyron equation becomes

$$\frac{dP}{dT} = \frac{\Delta_{fus}\bar{H}}{T \Delta_{fus}\bar{V}}$$

At a pressure of one bar and a temperature of 273.15 K, the enthalpy of fusion is $6010 \text{ J mol}^{-1} \text{ K}^{-1}$. The enthalpy value changes only slowly as the equilibrium temperature changes. The volumes of one mole of ice and one mole of water are 19.651 and 18.019 cm^3 , respectively. At 273.15 K, we obtain

$$\frac{dP}{dT} = -143.7 \text{ bar K}^{-1}$$

If the pressure increases to 1000 bar, the change in the melting point is about -6.96 K, so that $T_{mp}(1000 \text{ bar}) = 266.2$ K.

Again, this analysis is successful because the constituents are pure phases; the properties of the ice are independent of how much water is present and *vice versa*. When we analyze the equilibrium between ice and salt water, the properties of the salt water depend on the kind of salt present and on its concentration.

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