

# Free energy dependence along the coexistence curve

In a system where two phases (e.g. liquid and gas) are in equilibrium the Gibbs energy is  $G = G^{\ell} + G^g$ , where  $G^{\ell}$  and  $G^g$  are the Gibbs energies of the liquid phase and the gas phase, respectively. If  $dn$  moles (a differential amount of  $n$  the number of moles) are transferred from one phase to another at constant temperature and pressure, the differential Gibbs energy for the process is:

$$dG = \left( \frac{\partial G^g}{\partial n^g} \right) dn^g + \left( \frac{\partial G^{\ell}}{\partial n^{\ell}} \right) dn^{\ell}$$

The rate of change of free energy with number of moles is called the chemical potential.

# Free energy dependence along the coexistence curve

At the phase boundary between liquid and water we can write the free energy change as:

$$dG = \left( \frac{\partial G^g}{\partial n^g} \right) dn^g + \left( \frac{\partial G^\ell}{\partial n^\ell} \right) dn^\ell$$

The rate of change of free energy with number of moles is called the chemical potential.

$$\mu^g = \left( \frac{\partial G^g}{\partial n^g} \right)$$

# The significance of chemical potential of coexisting phases

We can write the Gibbs free energy change using the following notation:

$$dG = \mu^g dn^g + \mu^l dn^l$$

Note that if the system is entirely composed of gas molecules the chemical potential  $\mu^g$  will be large and  $\mu^l$  will be zero. Under these conditions the number of moles of gas will decrease  $dn^g < 0$  and the number of moles of liquid will increase  $dn^l > 0$ . Since every mole of gas molecules converted results in a mole of liquid molecules we have that:

$$dn^g = -dn^l$$

# Coexistence criterion

In terms of chemical potential, the Gibbs energy for the phase equilibrium is:

$$dG = (\mu^g - \mu^l)dn^g$$

Since the two phases are in equilibrium  $dG = 0$  and since  $dn^g \neq 0$  we have  $\mu^g = \mu^l$ . In plain language, if two phases of a single substance are in equilibrium their chemical potentials are equal.

If the two phases are not in equilibrium a spontaneous transfer of matter from one phase to the other will occur in the direction that minimizes  $dG$ . Matter is transferred from a phase with higher chemical potential to a phase with lower chemical potential consistent with the negative sign of Gibb's free energy for a spontaneous process.

# Solid-liquid coexistence curve

To derive expressions for the coexistence curves on the phase diagram we use the fact that the chemical potential is equivalent in the two phases. We consider two phases  $\alpha$  and  $\beta$  and write

$$\mu^\alpha(T,P) = \mu^\beta(T,P)$$

Now we take the total derivative of both sides

$$\left(\frac{\partial \mu^a}{\partial P}\right) dP + \left(\frac{\partial \mu^a}{\partial T}\right) dT = \left(\frac{\partial \mu^b}{\partial P}\right) dP + \left(\frac{\partial \mu^b}{\partial T}\right) dT$$

The appearance of this equation is quite different from previous equations and yet you have seen this equation before. The reason for the apparent difference is the symbol  $\mu$ , which is just the molar free energy.

# The Clapeyron equation

Substituting these factors into the total derivative above we have

$$V_m^a dP - S_m^a dT = V_m^b dP - S_m^b dT$$

Solving for  $dP/dT$  gives

$$\frac{dP}{dT} = \frac{S_m^b - S_m^a}{V_m^b - V_m^a} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T \Delta V_m}$$

This equation is known as the Clapeyron equation. It gives the two-phase boundary curve in a phase diagram with  $\Delta_{\text{trs}} H$  and  $\Delta_{\text{trs}} V$  between them. The Clapeyron equation can be used to determine the solid-liquid curve by integration.

# Integrated Clapeyron equation

Think of  $dP/dT$  as the slope of a curve in  $T,P$  space.

Temperature and pressure are the variables of the phase diagram:

$$\frac{dP}{dT} = \frac{\Delta H_m}{T \Delta V_m}$$

The integrals needed to make this useful are:

$$\int_{P_1}^{P_2} dP = \frac{\Delta H_m}{\Delta V_m} \int_{T_1}^{T_2} \frac{dT}{T}$$

The slope  $\Delta H_m/\Delta V_m$  involves molar changes in enthalpy and volume.

# Integrated Clapeyron equation

The integrated equation is:

$$P_2 - P_1 = \frac{\Delta H_m}{\Delta V_m} \ln \left( \frac{T_2}{T_1} \right)$$

Starting with a known point along the curve (e.g. the triple point or the melting temperature at one bar) we can calculate the rest of the curve referenced to this point.

This equation has applications such as understanding ice skating, which uses the melting of water underneath the pressure of sharp blades or erosion due to the pressure of ice that forms in cracks of rocks.



# The liquid-vapor and solid-vapor coexistence curves

The Clapeyron equation cannot be applied to a phase transition to the gas phase since the molar volume of a gas is a function of the pressure. We return to the equation:

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T \Delta V_m}$$

Making the assumption that  $V_m^g \gg V_m^l$  we can use the ideal gas law to obtain a new expression for  $dP/dT$ .

$$\frac{dP}{dT} = \frac{\Delta H_m}{T \left( \frac{RT}{P} \right)}$$

# Justification for use of ideal gas

We can easily justify the assumption that  $V_m^g \gg V_m^l$ . If we think about liquid water near its boiling point, we can calculate

$$V_m^l = \frac{M}{\rho}$$

where  $M$  is the molar mass and  $\rho$  is the density. Here  $M = 18$  grams/mole and  $\rho = 1$  gram/cm<sup>3</sup>. Thus,  $V_m^l = 18$  cm<sup>3</sup>/mole or 0.018 L/mole. For the vapor we have

$$V_m^g = \frac{RT}{P} = \frac{\left(0.08206 \frac{L \cdot atm}{mol \cdot K}\right) (373 K)}{1 atm} = 30.6 L$$

# Vapor coexistence curves

Rearranging the expression we find:

$$\frac{dP}{dT} = \frac{\Delta H_m P}{RT^2}$$

Next we arrange the equation so the variables of P are on one side and those of T are on the other.

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta H_m}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

# Clausius-Clapeyron equation

Finally we integrate the equation:

$$\ln \left( \frac{P_2}{P_1} \right) = - \frac{\Delta H_m}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

If we use  $\Delta H$  of evaporation the C-C equation can be used to describe the liquid-vapor coexistence curve and if we use  $\Delta H$  of sublimation this equation can be used to describe the solid-vapor curve.

Use  $\Delta_{vap}H_m$  for the liquid-vapor curve

Use  $\Delta_{sub}H_m$  for the solid-vapor curve

# Applying the Clausius-Clapeyron equation

The pressure derived from the C-C equation is the vapor pressure at the given temperature. Applications also include determining the pressure in a high temperature vessel containing a liquid (e.g. a pressure cooker). If you are given an initial set of parameters such as the normal boiling point, for example you may use these as  $T_1$  and  $P_1$ . Then if you are given a new temperature  $T_2$  you can use the C-C to calculate  $P_2$ .