Phase Equilibria

9.1 The Clausius-Clapeyron Equation

Let us consider two phases in equilibrium, like liquid and vapour.

Since we are at equilibrium, both phases have the same temperature T and pressure P.

We recall that the Gibbs free energy G = U - TS + PV ➡ G = G(T,P)

When liquid and vapour are in temperature and pressure equilibrium with its surroundings, G is at a minimum.

Now consider the specific Gibbs free energies of the phases, i.e. G per unit mass or per mole, g_1 and g_2 (where m is the mass or number of moles). We can write:

$$G = m_1 g_1 + m_2 g_2$$

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Let us consider an infinitesimal variation of G:

$$dG = m_1 \, dg_1 + m_2 \, dg_2 + g_1 \, dm_1 + g_2 \, dm_2$$

Since T and P are constant, and g = g(T, P), we have $dg_1 = dg_2 = 0$

$$dG = g_1 \, dm_1 + g_2 \, dm_2$$

$dm_1 = -dm_2$, from conservation of mass, so, at equilibrium dG = 0, we have:

$$g_1 = g_2$$

two phases are in equilibrium
if their specific Gibbs free energies are the same

It is useful to consider cases of constant T and P,
since typically V changes in phase transitions

We have shown that: $g_1 = g_2$

Now let's consider what happens if we alter T and P:

$$\mathrm{d}g_1 = \mathrm{d}g_2$$

But we know that: $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P$

If we consider specific quantities, we can rewrite it as:

$$-s_1\,\mathrm{d}T + v_1\,\mathrm{d}P = -s_2\,\mathrm{d}T + v_2\,\mathrm{d}P,$$

where s_1, v_1, s_2, v_2 are the specific entropies and volumes of the two phases, i.e. per unit mass or per mole

$$-s_1\, \mathrm{d}T + v_1\, \mathrm{d}P = -s_2\, \mathrm{d}T + v_2\, \mathrm{d}P,$$

in order to maintain equilibrium between the phases, a change in temperature must be matched by a change in pressure.
Therefore we can work out the rate of change of pressure with temperature which is:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{s_2 - s_1}{v_2 - v_1}$$

If we consider the latent heat L, it converts mass between phase 1 and 2:

$$s_2 - s_1 = \frac{L}{T}$$

Clausius-Clapeyron equation

$$\boxed{\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L}{T(v_2 - v_1)}}$$

Clausius-Clapeyron equation

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L}{T(v_2 - v_1)}$$

It describes how

the vapour pressure of a liquid changes with temperature

how the melting point of solids and the boiling point of

liquids changes with pressure.

9.1.1 Melting point of ice

Let us consider water and ice:

the latent heat of fusion of ice is L = 335 10³ J kg⁻¹
the specific volumes are
$v_2 = v_W = 10^{-3}$ m³ kg⁻¹
$v_1 = v_I = 1.09 \ 10^{-3}$ m³ kg⁻¹
for water and ice respectively (note that ice is less dense than water and hence has a larger specific volume).
Putting these figures into the Clausius-Clapeyron equation gives:

$$\frac{dP}{dT} = \frac{335 \times 10^3 \,\mathrm{J\,kg^{-1}}}{273\,\mathrm{K} \times (1.00 - 1.09) \times 10^{-3}\,\mathrm{m^3\,kg^{-1}}} = -13.6 \times 10^6 \,\mathrm{N\,m^{-2}\,K^{-1}}$$

This equations shows that if the external pressure increases by 134 atmospheres, the melting point of ice drops by 1 K.
It is the fact that ice is less dense than water that determines the sign of the change. Most solids are denser than their equivalent liquids and their melting point increases with pressure.

9.1.2 Boiling Point of Water

The latent heat of evaporation of water is L = 2.257 $\times$ 10^6 J kg^{-1}, while the specific volumes of steam and water are
$v_2 = v_S = 1.673$m^3 kg^{-1} and $v_1 = v_W = 1.043 \times 10^{-3}$ m^3 kg^{-1}, so:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{2.257 \times 10^6}{373(1.673 - 1.043 \times 10^{-3})} = 3619\,\mathrm{N\,m^{-2}\,K^{-1}}$$

This shows the rate at which the vapour pressure of water increases with temperature.

Alternatively, given that the boiling point is defined by the point at which the vapour pressure of a liquid equals the surrounding atmospheric pressure, this equation can tell you how the boiling point changes with pressure.

9.2 Supersaturation

Consider cooling a vapour down.

At some point when its pressure matches the saturated vapour pressure for the temperature in question, one expects condensation to occur.

However, this is not always the case, and the vapour can carry on without condensation down to cooler temperatures, at least for a while.

It is then known to be supersaturated

To see why this can happen we have to look at the vapour pressure of small droplets which turns out to be higher than that of a flat liquid surface.

The reason is to do with surface tension

Surface tension is a force that acts on the surfaces of liquids and is measured in terms of a force per unit length, γ.

Now consider a spherical liquid drop of radius r.
Around its equator surface tension provides a force of: $2\pi r \gamma$

Opposing this is a pressure P acting over the cross-sectional area of the drop πr^2, therefore:

$$\pi r^2 \Delta P = 2\pi r \gamma$$

and so surface tension raises the pressure inside a drop of radius r by:

$$\Delta P = \frac{2\gamma}{r}$$

This increase of pressure changes the specific Gibbs free energy of the liquid g_l, and therefore there has to be a compensating increase in vapour pressure.
From the equation for dG, at fixed temperature g_l is increased by $g_l = v_l P$, where v is a specific volume, and therefore g_v must increase by the same amount so:

$$\Delta g_v = v_v \Delta P_v = v_l \Delta P.$$

As a result the vapour pressure of a droplet of radius r is larger than that of a flat surface at the same temperature by an amount:

$$\Delta P_v = \frac{v_l}{v_v} \frac{2\gamma}{r}$$

It is this which allows vapours to be supersaturated

because the saturated vapour pressure of droplets is such that they will not form until higher pressures than the normal saturated vapour pressure of a liquid surface are reached.

Since droplets have to start from a tiny radius, it is rather difficult to see how condensation happens as easily as it often does.
The reason is thought to be the presence of condensation nuclei, such as charged particles and dust. The attractive forces of these lower g_l enough for condensation to get going.

9.3 Summary

applications of Gibbs Free Energy
to the equilibrium of chemical reactions

Clausius-Clapeyron equation

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L}{T(v_2 - v_1)}$$

o Melting point of ice

o Boiling point of water

o Supersaturation