

# STATISTICAL MOLECULAR THERMODYNAMICS

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Video 9.5

Chemical Potentials and the Clapeyron Equation

# FREE ENERGY OF A TWO-PHASE SYSTEM

The Gibbs energy of two phases in equilibrium with one another — we'll use gas (*g*) and liquid (*l*) here for convenience, but the equations are general — is simply the sum of the individual phase's Gibbs free energies:

$$G = G^g + G^l$$

Now, consider transfer of  $dn$  moles from the liquid phase to the gas phase with  $T$  and  $P$  kept constant. The change in the Gibbs energy is:

$$dG = \left( \frac{\partial G^g}{\partial n^g} \right)_{P,T} dn^g + \left( \frac{\partial G^l}{\partial n^l} \right)_{P,T} dn^l$$

# FREE ENERGY OF A TWO-PHASE SYSTEM

Change in Gibbs free energy with phase transfer:

$$dG = \left( \frac{\partial G^g}{\partial n^g} \right)_{P,T} dn^g + \left( \frac{\partial G^l}{\partial n^l} \right)_{P,T} dn^l$$

But mass balance dictates:  $dn^g = -dn^l$

So we have:

$$dG = \left[ \left( \frac{\partial G^g}{\partial n^g} \right)_{P,T} - \left( \frac{\partial G^l}{\partial n^l} \right)_{P,T} \right] dn^g$$

## CHEMICAL POTENTIAL DEFINED

$$dG = \left[ \left( \frac{\partial G^g}{\partial n^g} \right)_{P,T} - \left( \frac{\partial G^l}{\partial n^l} \right)_{P,T} \right] dn^g$$

The partial derivatives above are called partial molar Gibbs free energies or, more commonly, *chemical potentials*,  $\mu$ , where:

$$\mu^i = \left( \frac{\partial G^i}{\partial n^i} \right)_{P,T}$$

in which case we write:  $dG = [\mu^g - \mu^l] dn^g$

## PHASE TRANSFERS

$$dG = [\mu^g - \mu^l] dn^g$$

At equilibrium,  $dG = 0$  — this will be true if  $\mu^g = \mu^l$

If  $\mu^g > \mu^l$ , then  $dG < 0$  (spontaneous change) iff  $dn^g < 0$ , i.e., matter transfers from gas phase to liquid phase

If  $\mu^g < \mu^l$ , then  $dG < 0$  (spontaneous change) iff  $dn^g > 0$ , i.e., matter transfers from liquid phase to gas phase

Out of equilibrium, matter flows from a higher chemical potential to a lower chemical potential

# PHASE CHANGE CHARACTERISTICS

For a pure substance, the chemical potential is simply the molar Gibbs energy, an intensive quantity (i.e., like  $T$  and  $P$ ).

$$\mu^i = \left( \frac{\partial G^i}{\partial n^i} \right)_{P,T} = \bar{G}^i$$

At equilibrium:  $\mu^\alpha(T, P) = \mu^\beta(T, P)$  so we may write:

$$\left( \frac{\partial \mu^\alpha}{\partial P} \right)_T dP + \left( \frac{\partial \mu^\alpha}{\partial T} \right)_P dT = \left( \frac{\partial \mu^\beta}{\partial P} \right)_T dP + \left( \frac{\partial \mu^\beta}{\partial T} \right)_P dT$$

or, equivalently:

$$\left( \frac{\partial \bar{G}^\alpha}{\partial P} \right)_T dP + \left( \frac{\partial \bar{G}^\alpha}{\partial T} \right)_P dT = \left( \frac{\partial \bar{G}^\beta}{\partial P} \right)_T dP + \left( \frac{\partial \bar{G}^\beta}{\partial T} \right)_P dT$$

## THE CLAPEYRON EQUATION

$$\left(\frac{\partial \bar{G}^{\alpha}}{\partial P}\right)_T dP + \left(\frac{\partial \bar{G}^{\alpha}}{\partial T}\right)_P dT = \left(\frac{\partial \bar{G}^{\beta}}{\partial P}\right)_T dP + \left(\frac{\partial \bar{G}^{\beta}}{\partial T}\right)_P dT$$

may be rewritten:  $\bar{V}^{\alpha} dP - \bar{S}^{\alpha} dT = \bar{V}^{\beta} dP - \bar{S}^{\beta} dT$

which rearranges to: 
$$\frac{dP}{dT} = \frac{\bar{S}^{\beta} - \bar{S}^{\alpha}}{\bar{V}^{\beta} - \bar{V}^{\alpha}} = \frac{\Delta_{\text{trs}} \bar{S}}{\Delta_{\text{trs}} \bar{V}} = \frac{\Delta_{\text{trs}} \bar{H}}{T \Delta_{\text{trs}} \bar{V}}$$

*cf. video 7.3*

The Clapeyron equation relates the slope of the coexistence curve ( $dP/dT$ ) to the changes in molar enthalpy and volume associated with a phase change

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

# Self-assessment

At its standard melting point, water has an enthalpy of fusion of 6.01 kJ/mol and a volume of fusion of  $-1.63 \text{ cm}^3/\text{mol}$ . Using the Clapeyron equation (below), predict the melting point of water at 1000 bar pressure.

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



# Self-assessment Explained

We can invert the Clapyeron equation to compute how temperature should vary with pressure, using the data for water at its standard melting point (273.15 K, 1 bar), thus:

$$\begin{aligned}\frac{dT}{dP} &= \frac{T \Delta_{\text{trs}} \bar{V}}{\Delta_{\text{trs}} \bar{H}} = \frac{(273.15 \text{ K}) (-1.63 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1})}{6010 \text{ J mol}^{-1}} \cdot \left( \frac{0.01 \text{ J bar}^{-1}}{1 \text{ dm}^3} \right) \\ &= -7.41 \times 10^{-3} \text{ K bar}^{-1}\end{aligned}$$

So a pressure increase of 999 bar should lower the melting point by 7.40 K. Experiment gives 9.3 K. The error derives from our assumption that the transition enthalpy and volume are independent of temperature, implicit in the Clapeyron equation.

$$dU = \delta q + \delta w$$



*Next: Clausius-Clapeyron Equation*