Lecture 24  Chapt 14  Clausius-Clapeyron Equation

Announcements:

We’ll review for exam this afternoon – no quiz this week.

Outline:

Clapeyron Equation
\[ \frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H}{T \Delta V} \]

Clausius – Clapeyron Equation
\[ \frac{1}{p} \frac{dp}{dT} = \frac{\Delta_{\text{trans}} H}{nRT^2} \]
\[ \ln(p) = -\frac{\Delta_{\text{trans}} H}{RT} + \text{constant} \]

Review

Phase Diagrams Summarize Solid-Liquid-Gas Behavior of a Substance

\[ \left( \frac{\partial G}{\partial p} \right)_T = V \quad \text{and} \quad \left( \frac{\partial G}{\partial T} \right)_p = -S \quad \text{(equating coefficients in expressions for dG)} \]

Therefore, if we plot \( G \) vs. \( T \), what is the slope? negative of the (molar) entropy

![Phase Diagram](image)

If we repeat for many pressures, then we can build up a full phase diagram – a \( P \) vs. \( T \) plot showing regions of thermodynamic stability. We have a generic one below:
Let’s look at phase transitions a little more quantitatively.

**Equilibrium:** $\Delta G$ must be 0, so between two phases, $\alpha$ and $\beta$: $\mu_\alpha(p,T) = \mu_\beta(p,T)$

Therefore, there is no thermodynamic driving force for change

We can use this equality to get an equation for the phase boundary.

If $p$ and $T$ are changed infinitesimally in a way that the two phases $\alpha$ and $\beta$ remain in equilibrium. Then

$\mu_\alpha = \mu_\beta \quad$ before the change

$\mu_\alpha + d\mu_\alpha = \mu_\beta + d\mu_\beta \quad$ after the change

and therefore

$d\mu_\alpha = d\mu_\beta \quad$ (or equivalently for two phases of a pure substance)

$dG_{\alpha,m} = dG_{\beta,m}$

plug in (fundamental equation?!) $dG_m = -S_m dT + V_m dp$ for each phase:

$-S_{\alpha,m}dT + V_{\alpha,m}dp = -S_{\beta,m}dT + V_{\beta,m}dp$ and this rearranges

$(V_{\beta,m} - V_{\alpha,m})dp = (S_{\beta,m} - S_{\alpha,m})dT$

For measurable changes, this expression becomes the **Clapeyron Equation**:

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

**Notice that this is a total derivative and applies for any phase change for any pure substance.**
Let’s see a quick example:
How does the vapor pressure for water change as its temperature is changed?

\[
\Delta S_m = \Delta_{\text{trans}}S_m = S_m (\beta) - S_m (\alpha) = 188.8 \text{ J K}^{-1} \text{ mol}^{-1} - 69.9 \text{ J K}^{-1} \text{ mol}^{-1} = 118.9 \text{ J K}^{-1} \text{ mol}^{-1}
\]

\[
\Delta V_m = \Delta_{\text{trans}}V_m = V_m (\beta) - V_m (\alpha) \approx V_m (\beta) = \frac{RT}{p} = 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} / 24 \text{ Torr} = 103 \text{ J mol}^{-1} \text{ torr}^{-1}
\]

\[
\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{118.9 \text{ JK}^{-1} \text{ mol}^{-1}}{103 \text{ Jmol}^{-1} \text{ Torr}} = 1.15 \text{ Torr K}^{-1}
\]

So at 10 °C, the vapor pressure is 24 Torr + 1.15 Torr K^{-1} x (-15 K) = 6.75 Torr

**Molecular explanation for why \( \frac{dp}{dT} \) is always positive:** higher T means more energy available for molecules to escape attractive forces in liquid

**What is vapor pressure at 1 °C?** 25 torr + 1.15 torr/K (-24 K) = -3.6 torr.

**What is wrong?** You can’t use this expression very far from the reference temperature (298 K in this case) because the \( \Delta S/\Delta V \) ratio changes with temp.

For two phases at equilibrium we can change the Clapeyron eq by noting:

\[
G_\alpha = G_\beta
\]

\[
H_\alpha - TS_\alpha = H_\beta - TS_\beta
\]

\[
T(S_\beta - S_\alpha) = H_\beta - H_\alpha
\]

\[
T\Delta_{\text{trans}}S = \Delta_{\text{trans}}H
\]

\[
\Delta_{\text{trans}}S = \Delta_{\text{trans}}H / T \quad (\text{This should look familiar} \ldots \text{when } \Delta_{\text{trans}}H = q)
\]

We then can rewrite the Clapeyron equation:

\[
\frac{dp}{dT} = \frac{\Delta_{\text{trans}}H}{T\Delta_{\text{trans}}V}
\]

If we make two assumptions:

1) \( \Delta_{\text{trans}}V = V_{\text{gas}} - V_{\text{liquid}} \) (or \( V_{\text{solid}} \)) \( \approx V_{\text{gas}} \) (volume of liquid or solid is negligible)

2) \( V_{\text{gas}} = nRT/p \) (ideal gas)

\[
\frac{dp}{dT} = \frac{p\Delta_{\text{trans}}H}{nRT^2} \quad \text{we know how to solve this.} \quad \text{Rearranging to get common variables on the same side of the equation}
\]
\[
\frac{dp}{p} = \frac{\Delta_{\text{trans}}H_m}{R} \times \frac{dT}{T^2}
\]

This is one form of the Clausius-Clapeyron eq.

If we integrate both sides indefinitely

\[
\int \frac{dp}{p} = \int \frac{\Delta_{\text{trans}}H_m}{R} \times \frac{dT}{T^2}
\]

\[
\ln p = \frac{\Delta_{\text{trans}}H_m}{R} \left( -\frac{1}{T} \right) + \text{constant}
\]

Second form of the Clausius-Clapeyron eq.

Thus, this tells us that a plot of \( \ln p \) vs \( 1/T \) is linear with slope = \( -\Delta_{\text{trans}}H_m/R \)

what do we assume here? That \( \Delta_{\text{trans}}H_m \) is constant

If instead, we do the integral definitely (from \( p_1, T_1 \) to \( p_2, T_2 \)):

\[
\int_{p_1}^{p_2} \frac{dp}{p} = \frac{\Delta_{\text{trans}}H_m}{R} \times \int_{T_1}^{T_2} \frac{dT}{T^2}
\]

\[
\ln \left( \frac{p_2}{p_1} \right) = -\frac{\Delta_{\text{trans}}H_m}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

Yet a third form of the Clausius-Clapeyron eq.

Before next time, let's review the different ways of reporting the composition of a solution:

**Molarity (M):** moles of solute per liter of solution.

**Molality (m):** moles of solute per kg of solvent (H₂O).

**Mole fraction (X):** moles of solute per total moles of solute and solvent

**Weight fraction (w):** mass of solute per total mass of solute and solvent

All 4 of these conventions are in popular use!

Recall that for gases, we used Dalton’s law \( (p_i = X_i p_{\text{tot}}) \) to calculate the partial pressures. This is valid for mixtures that behave ideally. Clearly, molecules are obviously interacting with each other in the liquid phase, can we use something similar to Dalton’s law for liquid mixtures? We’ll get into this on Monday

Rather than plow into something new right before you forget about it by cramming for the exam, we’ll stop for today.