Phase boundaries

Vapor pressure

At phase boundary: Dynamic equilibrium between two phases
\[ \Delta G = 0 \]
Phase boundaries: Where are they?

Phase 1: \[ dG_m(1) = V_m(1)dp - S_m(1)dT \]
Phase 2: \[ dG_m(2) = V_m(2)dp - S_m(2)dT \] \} in equilibrium

Along the phase boundary, the molar Gibbs energies stay equal
⇒ the changes in their molar Gibbs energies must be equal

\[ V_m(1)dp - S_m(1)dT = V_m(2)dp - S_m(2)dT \]

⇒ \[ [S_m(2) - S_m(1)]dT = [V_m(2) - V_m(1)]dp \]

\( \Delta_{trs}S \)
\( \Delta_{trs}V \)

\( \frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V} \)

Clapeyron equation
Special case: The liquid-vapor boundary

\[
\begin{align*}
\frac{dp}{dT} &= \frac{\Delta_{vap} S}{\Delta_{vap} V} = \frac{\Delta_{vap} H}{T\Delta_{vap} V} = \frac{\Delta_{vap} H}{TV_m(g)} = \frac{\Delta_{vap} H}{T(RT/p)} = p\frac{\Delta_{vap} H}{RT^2} \\
\text{trs} \rightarrow \text{vap} \quad \Delta_{vap} S &= \Delta_{vap} H/T \\
\Delta_{vap} V &= V_m(g); \text{ approximation} \\
V_n(l) &\text{ small}
\end{align*}
\]

\[
\text{Slope} = \frac{\Delta_{vap} H}{RT^2}
\]

\[
\frac{d\ln p}{dT} = \frac{\Delta_{vap} H}{RT^2}
\]

**Clausius-Clapeyron equation**

\[
\int_{p}^{p'} d\ln p = \int_{T}^{T'} \frac{\Delta_{vap} H}{RT^2} dT
\]

\[
\Rightarrow \ln \left( \frac{p'}{p} \right) = \frac{\Delta_{vap} H}{R} \left( \frac{1}{T} - \frac{1}{T'} \right)
\]
Characteristic points

Same as melting point; “normal” = at 1 atm

Closed vessel:
Pressure increases until critical point is reached \((T_c, p_c)\);
phase boundary is lost

Open vessel:
Vapor pressure equals external pressure ⇒ vapor drives back atmosphere: Boiling

Highest T for liquid

Lowest T for liquid

Only set of conditions where all three phases coexist (water: 273.16 K, 611 Pa)
How many phases can coexist in equilibrium?

Four phases: $G_m(1) = G_m(2); G_m(2) = G_m(3); G_m(3) = G_m(4)$

BUT: Only two unknown parameters ($p, T$) in a phase diagram

$\Rightarrow$ Four phases cannot coexist in equilibrium!

Phase rule: $F = C - P + 2$

$F =$ Number of degrees of freedom

$C =$ number of components

$P =$ number of phases
Phase diagrams: Water

Liquid water has a higher density than water ice

On Mt. Everest “boiling” eggs becomes easier
Phase diagrams: CO$_2$ and Helium

CO$_2$: quite typical

- Sublimes at 1 atm; exists as a liquid only under pressure
- Solid
- Liquid
- Gas

He: solid and gas are never in equilibrium; He-II is superfluid

- Solid
- Liquid I
- Gas
- Liquid II (superfluid)

- 72.8 bar, 304 K
- 5.11 bar, 217 K
- 1 bar, 195 K
- 67 bar, 298 K
- 2.3 bar, 5.2 K
- 2.2 K

Nils Walter: Chem 260