Statistical Molecular Thermodynamics

Christopher J. Cramer

Video 9.1

Phase Equilibria and Phase Diagrams
Phase Diagram

A phase diagram indicates the equilibrium phase of matter of a pure substance given specification of a pressure \((P)\) and a temperature \((T)\) “state point”.

The “coexistence curves” in the phase diagram indicate the equilibrium co-existence of *multiple* phases.

The triple point is the precise state point at which solid, liquid, and gas all co-exist at equilibrium.
Using log(P) in place of P often more convenient when a large temperature range is under consideration — note the effect on the curvature of the solid-gas and liquid-gas coexistence curves.
Self-assessment

The vapor pressure above solid CO$_2$ can be described by the equation:

$$\ln\left(\frac{P}{\text{Pa}}\right) = -\frac{3125}{T} + 27.58$$

And the vapor pressure above liquid CO$_2$ can be described by the equation:

$$\ln\left(\frac{P}{\text{Pa}}\right) = -\frac{2011}{T} + 22.44$$

What is the temperature and pressure of a closed volume of CO$_2$ that contains solid, liquid, and gas at equilibrium? While this problem uses units of Pa — what is the pressure in atmospheres, also?
Self-assessment Explained

At the triple-point (all phases present), both vapor pressure equations must hold and give the same pressure, thus we can set them equal to one another and solve for $T_{\text{triple-point}}$:

$$\frac{-3125}{T_{\text{triple-point}}} + 27.58 = -\frac{2011}{T_{\text{triple-point}}} + 22.44$$

Some quick algebra gives $T_{\text{triple-point}} = 216.73$ K which, when plugged into either vapor pressure equation, permits computation of $P_{\text{triple-point}} = 519820$ Pa, or about 5.1 atm.

(You can revisit the CO$_2$ triple-point demo and now you’ll know the pressure inside the soda bottle!)
"Dry" Ice Sublimes Instead of Melting

If 1 atm is below the triple point on a given phase diagram, the substance will sublime rather than melt at 1 atm (CO$_2$ triple point is 5.11 atm)
The Gibbs Phase Rule

\[ f = 3 - p \]

- \( f \) = “degrees of freedom” \((P\ \text{and/or}\ T)\)
- \( p \) = number of phases present \((1, 2, \text{or } 3)\)

Note that the coexistence curves describe the pressure dependence of a phase transition.
**Boiling and Melting as Function of **$T$

At 1 atm the boiling point is 80.1 °C  
At 500 torr the boiling point is 67 °C

BP at 1 atm = **Normal boiling point**  
BP at 1 bar = **Standard boiling point**

At 1 atm the melting point is 5.5 °C (**normal**)  
At 34 atm the melting point is 6.5 °C

slope $\approx 0.0293$ °C $\cdot$ atm$^{-1}$ (**insensitive**)  

MP at 1 atm = **Normal melting point**  
MP at 1 bar = **Standard melting point**

(1 torr = $1.33 \times 10^{-3}$ bar = 1/760 atm)

Note different units of pressure
\[ dU = \delta q + \delta w \]

Next: Phase Diagram for Water