Statistical Molecular Thermodynamics

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Video 9.6

Clausius-Clapeyron Equation
The transition volume of a gas is very sensitive to temperature and pressure, so using a fixed value is not very effective for computing sublimation or vaporization behavior. Further manipulation proves useful, however, making use of:

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

where the approximation follows from the molar volume of a gas typically being much larger than that for liquid or solid
The Clausius-Clapeyron Equation

\[
\frac{dP}{dT} = \frac{\Delta_{trs} \bar{H}}{T \Delta_{trs} \bar{V}} \approx \frac{\Delta_{trs} \bar{H}}{T \bar{V}^g} = \frac{P \Delta_{trs} \bar{H}}{RT^2}
\]

The final equality derives from using the ideal gas equation of state to substitute \( \bar{V} \) with \( RT / P \).

If we divide both sides by \( P \) we can write

\[
\frac{d \ln P}{dT} = \frac{\Delta_{trs} \bar{H}}{RT^2}
\]

For \( trs = \text{sub/vap} \)
Integrated form of the CC Equation

\[
\frac{d \ln P}{dT} = \frac{\Delta_{\text{trs}} \bar{H}}{RT^2}
\]

\[
\int_{P_1}^{P_2} d\ln P = \int_{T_1}^{T_2} \frac{\Delta_{\text{trs}} \bar{H}}{RT^2} dT
\]

where the latter equation integrates to

\[
\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{trs}} \bar{H}}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)
\]

Can be used to compute the vapor pressure at one temperature given the vapor pressure and transition enthalpy at another temperature.
Self-assessment

At its normal boiling point of 353.2 K, benzene has an enthalpy of vaporization of 30.8 kJ/mol. Using the integrated form of the Clausius-Clapeyron equation (below), predict the vapor pressure (torr) in a sealed vessel containing benzene that is immersed in boiling water.

\[
\ln \frac{P_2}{P_1} = \frac{\Delta_{trs} \bar{H}}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)
\]
Boiling water is 373.2 K (that will be $T_2$), and the normal boiling point ($T_1 = 353.2$ K) implies 1 atm ($P_1 = 760$ torr), thus

$$\ln \frac{P_2}{760} = \frac{30800 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{373.2 \text{ K} - 353.2 \text{ K}}{373.2 \cdot 353.2 \text{ K}^2} \right)$$

Solving for $P_2$ gives 1333 torr (experiment is 1360, with error again deriving from the heat of vaporization not being a constant independent of temperature)
Indefinite Integration of the CC Eq

\[ \frac{d \ln P}{dT} = \frac{\Delta_{\text{trs}} \bar{H}}{RT^2} \]

\[ \int d\ln P = \int \frac{\Delta_{\text{trs}} \bar{H}}{RT^2} dT \]

now offers:

\[ \ln P = -\frac{\Delta_{\text{trs}} \bar{H}}{R} \cdot \frac{1}{T} + C \]

Slope of \( \ln P \) vs \( 1/T \) permits determination of enthalpy of transition

Vapor pressure of liquid benzene from 313 K to 353 K

\[ \Delta_{\text{vap}} \bar{H} = 32.3 \text{ kJ} \cdot \text{mol}^{-1} \]
Accounting for $\Delta_{trs} \overline{H}(T)$

$$\int d\ln P = \int \frac{\Delta_{trs} \overline{H}}{RT^2} dT$$

Substitute: $\Delta_{trs} \overline{H} = a_0 + a_1 T + a_2 T^2 + \cdots$

Integration now yields:

$$\ln P = -\frac{a_0}{RT} + \frac{a_1}{R} \ln T + \frac{a_2}{R} T + C + O(T^2)$$

readily tabulated and useful over sizable ranges of $T$
Curvature In a Sublimation Example

\[ \text{NH}_3 (s) \rightarrow \text{NH}_3 (g) \]
\[ dU = \delta q + \delta w \]

Next: Chemical Potential from the Partition Function