

STATISTICAL MOLECULAR THERMODYNAMICS

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Video 9.6

Clausius-Clapeyron Equation

LIMITS OF THE CLAPEYRON EQUATION

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

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:

$$\Delta_{\text{trs}} \bar{V} = \bar{V}^g - \bar{V}^{l/s} \approx \bar{V}^g$$

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

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

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

For trs = sub/vap

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

*Clausius-Clapeyron
Equation*

INTEGRATED FORM OF THE CC EQUATION

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

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.

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

Self-assessment Explained

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

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

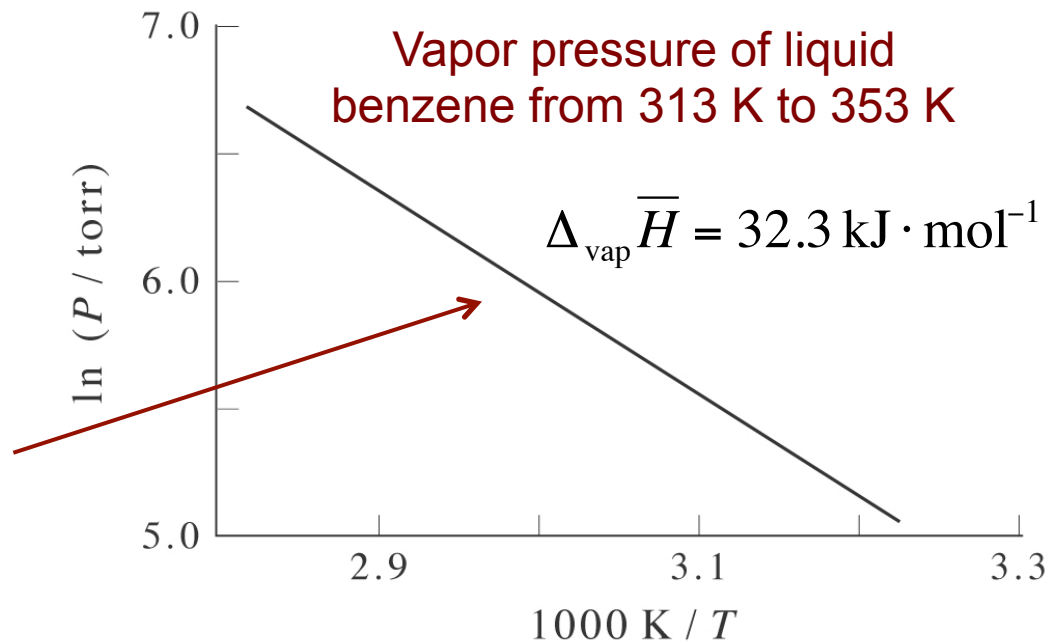


$$\int d \ln P = \int \frac{\Delta_{\text{trs}} \bar{H}}{RT^2} dT$$

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



ACCOUNTING FOR $\Delta_{\text{trs}}\bar{H}(T)$

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

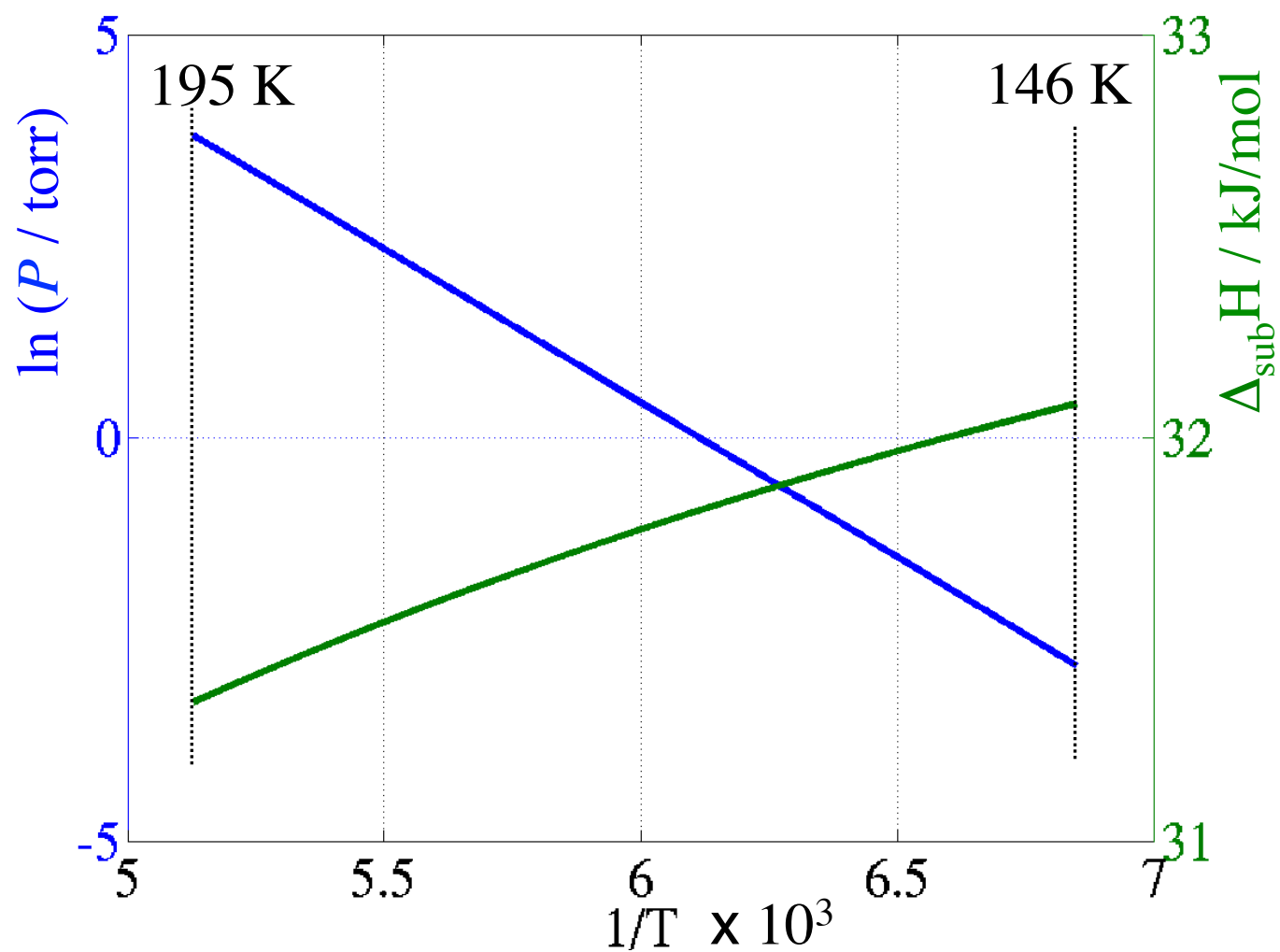
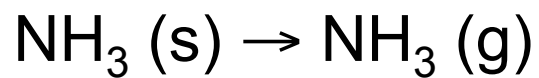
Substitute: $\Delta_{\text{trs}}\bar{H} = a_0 + a_1T + a_2T^2 + \dots$

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



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



Next: Chemical Potential from the Partition Function