

1. Clausius-Clapeyron Equation
2. Examples
3. Ch24: Partial Molar Quantities
4. Gibbs-Duhem Eq

Clapeyron eq $\frac{dp}{dT} = \frac{\Delta \bar{H}_{trans}}{T \Delta \bar{V}_{trans}}$

Water $s \rightleftharpoons l \Rightarrow \Delta \bar{V}_{trans} = \bar{V}_l - \bar{V}_s < 0$

$s \rightleftharpoons g$ sublimation $\Delta \bar{V}_{trans} = \bar{V}_g - \bar{V}_s$

$l \rightleftharpoons g$ vaporization $\Delta \bar{V}_{trans} = \bar{V}_g - \bar{V}_l$

$\bar{V}_g \gg \bar{V}_s, \bar{V}_l$

$\frac{dp}{dT} = \frac{\Delta \bar{H}_{trans}}{T \bar{V}_g} \leftarrow \left(\frac{RT}{P} \right)$

$\bar{V}_g \cdot P = RT$
 $\bar{V}_g = \frac{RT}{P}$

$\left(\frac{dp}{dT} \right) = \frac{\Delta \bar{H}_{trans} (P)}{RT^2}$

$\frac{1}{P} \cdot \frac{dp}{dT} = \frac{\Delta \bar{H}_{trans}}{RT^2} \Rightarrow \frac{d \ln P}{dT} = \frac{\Delta \bar{H}_{trans}}{RT^2}$ Clausius-Clapeyron eq

$\frac{d \ln x}{dx} = \frac{1}{x} \rightarrow d \ln x = \frac{1}{x} \cdot dx$

$\Delta \bar{H}_{trans}$ is independent of T

Integrated form of Clausius-Clapeyron

$\ln \frac{P_f}{P_i} = \frac{-\Delta \bar{H}_{trans}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$

Van't Hoff eq

$$\ln \frac{K_f}{K_i} = \frac{-\Delta H_{\text{tran}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

Example:

At 1 atm, benzene melts at 278.7 K .

$$\Delta \bar{H}_{\text{fus}} = 9.95 \text{ kJ/mol}, \quad \Delta \bar{V}_{\text{fus}} = 10.3 \frac{\text{cm}^3}{\text{mol}}$$

$$\frac{dP}{dT} = \frac{\Delta \bar{H}_{\text{fus}}}{T \Delta \bar{V}_{\text{fus}}} = 34.2 \text{ atm} \cdot \text{K}^{-1}$$

$$\frac{dT}{dP} = 0.03 \text{ K} \cdot \text{atm}^{-1}$$

predict T at 1000 atm?

$$278.7 \text{ K} + 0.03 \overset{29.97}{\cancel{(999)}} = \underline{\underline{308.67 \text{ K}}}$$

$$\text{exp value } T_{\text{melt}} = \underline{\underline{306.4 \text{ K}}}$$

why it's not exact?

1. slope is not changing

↳ $\Delta \bar{H}_{\text{trans}}$ is independent of T

↳ $\Delta \bar{V}_{\text{trans}}$ is ~ ~ of P

Benzene boils at 353.2 K at 1 atm and

$\Delta \bar{H}_{\text{vap}} = 30.8 \text{ kJ/mol}$, vapor P at 373.2 K ?

$$\ln \frac{P_2}{1 \text{ atm}} = \frac{-30.8 \text{ kJ/mol}}{R} \left(\frac{1}{373.2} - \frac{1}{353.2} \right)$$

$$P_2 = 1.754 \text{ atm} \quad P_2(\text{exp}) = \underline{\underline{1.789}}$$

still $\Delta \bar{H}_{\text{trans}}$ is considered to be T -independent.

ex: The vapor pressure of water is 1 atm at 373K, $\Delta \bar{H}_{\text{vap}} = 40.7 \frac{\text{kJ}}{\text{mol}}$. Estimate vapor P at $T = 363$?

$$\ln \frac{P_2}{P_1} = \frac{-\Delta \bar{H}_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = 0.697$$

\uparrow 1 atm \uparrow 8.314 $\frac{\text{J}}{\text{mol}\cdot\text{K}}$ \uparrow 363 \uparrow 373

ex: The vapor pressure of ice at 268K & 273K is 2.965 torr & 4.560 torr, respectively. Estimate the heat of sublimation for ice?

$$\ln \frac{2.965 \text{ torr}}{4.560 \text{ torr}} = \frac{-\Delta \bar{H}_{\text{sub}}}{8.314} \left(\frac{1}{268} - \frac{1}{273} \right)$$

$$\Delta \bar{H}_{\text{sub}} = 52.370 \frac{\text{kJ}}{\text{mol}}$$

Calculate the magnitude of the change in freezing point for water ($\Delta \bar{H}_{\text{fus}} = 6.009 \frac{\text{kJ}}{\text{mol}}$)

$\rho_{\text{ice}} = 0.9167 \frac{\text{g}}{\text{cm}^3}$ while that for

$\rho_{\text{water}} = 0.9999 \frac{\text{g}}{\text{cm}^3}$ for an increase in P of 1 atm at 273K.

$$\int \frac{dP}{dT} = \frac{\Delta \bar{H}_{\text{freezing}}}{T \Delta \bar{V}_{\text{freezing}}} \rightarrow \int dP = \frac{\Delta \bar{H}_{\text{freezing}}}{T \Delta \bar{V}_{\text{freezing}}} \cdot dT$$

$$\frac{dp}{dT} = \frac{\Delta \bar{H}_{\text{freez}}}{T \Delta \bar{V}_{\text{freez}}} \rightarrow \int_{T_1}^{T_2} T \Delta \bar{V}_{\text{freez}}$$

$$\Delta p = \frac{\Delta \bar{H}_{\text{freez}}}{\Delta \bar{V}_{\text{freez}}} \int_{T_1}^{T_2} \frac{dT}{T}$$

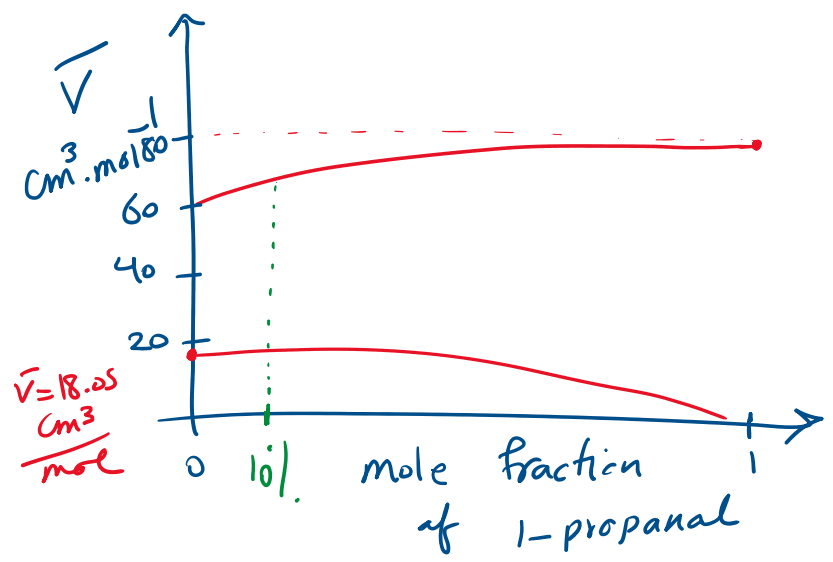
$T_2 = 273.1492 \text{ K}$

$$\Delta p = \frac{\Delta \bar{H}_{\text{freez}}}{\Delta \bar{V}_{\text{freez}}} \ln \left(\frac{T_2}{T_1} \right)$$

$\rho = \frac{m}{V}$ $\frac{18 \text{ g}}{\text{mol}}$

ch 24

mixture of water & 1-propanal



New quantities: partial molar quantities

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2$$

$$S = n_1 \bar{S}_1 + n_2 \bar{S}_2$$

$$\left\{ \begin{array}{l} S = n_1 \bar{S}_1 + n_2 \bar{S}_2 \\ G = n_1 \bar{G}_1 + n_2 \bar{G}_2 \end{array} \right.$$

$$dV = n_1 \cdot d\bar{V}_1 + dn_1 \cdot \bar{V}_1 + n_2 \cdot d\bar{V}_2 + dn_2 \cdot \bar{V}_2$$

at T, P is const $\left(\begin{array}{l} \frac{\partial V}{\partial n_1} \Big|_{T, P, n_2} \cdot dn_1 + \frac{\partial V}{\partial n_2} \Big|_{T, P, n_1} \cdot dn_2 \end{array} \right)$

$$dV = \left(\frac{\partial V}{\partial n_1} \right)_{T, P, n_2} \cdot dn_1 + \left(\frac{\partial V}{\partial n_2} \right)_{T, P, n_1} \cdot dn_2$$

$$dV = \bar{V}_1 \cdot dn_1 + \bar{V}_2 \cdot dn_2$$

$$n_1 \cdot d\bar{V}_1 + n_2 \cdot d\bar{V}_2 = 0$$

Gibbs-Duhem eq.

$\div n_{tot}$

$$\frac{n_1}{n_{tot}} \cdot d\bar{V}_1 + \frac{n_2}{n_{tot}} \cdot d\bar{V}_2 = 0$$

$$\left(\frac{n_1}{n_{\text{tot}}}\right) \cdot d\bar{V}_1 + \frac{\dots}{n_{\text{tot}}} \cdot d\bar{V}_2 = 0$$

$$x_1 \cdot d\bar{V}_1 + x_2 \cdot d\bar{V}_2 = 0$$

$$G = n_1 \bar{G}_1 + n_2 \bar{G}_2 = n_1 \mu_1 + n_2 \mu_2$$

$$\rightarrow dG = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2$$

$$G = G(T, p, n_1, n_2) \rightarrow dG = \mu_1 dn_1 + \mu_2 dn_2$$

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

$$x_1 d\mu_1 + x_2 d\mu_2 = 0$$

Gibbs-Duhem eq
for μ .