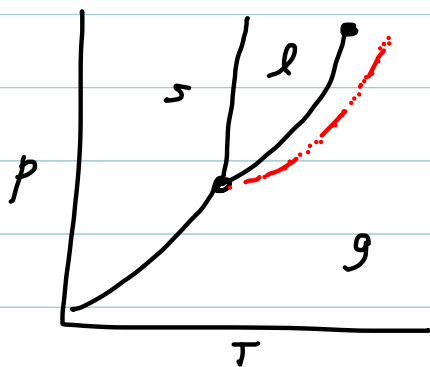


(L17) Colligative Properties - BP elevation proof

$\mu_{\text{SOLN}} < \mu_{\text{LIA}}$, but μ_{VAP} is the same after addition of solute



The result of this is BP elevation

If P is a confining pressure:

SOLV: $P = p^*$; SOLN: $P = p$

T_{bp} lower

T_{bp} higher

$p_{\text{solv}} > p_{\text{soln}}$ at all temperatures

$$K_b = \frac{M_A R (T^*)^2}{\Delta_{\text{vap}} H}$$

PROVE: $\Delta T_b = K_b b$
 change in bp ebullioscopic constant molality

AT EQB:
 $\mu_A(l) = \mu_A^*(g) = \mu_A^0(g)$
 $\mu_A(l) = \mu_A^0(l) + RT \ln x_A$

At eqb: $\mu_A^0(g) = \mu_A^0(l) + RT \ln x_A$

1 mol, $\mu^0 = G^0$

$$\frac{G_A^0(g) - G_A^0(l)}{T} = R \ln x_A$$

diff. wrt T : $\left(\frac{\partial(G(T))}{\partial T}\right)_P = -\frac{H^\circ}{T^2}$ (Gibbs-Helmholtz)

$$= -\frac{H_A^\circ(g) + H_A^\circ(l)}{T^2} = R \frac{d}{dT} (\ln x_A) \leftarrow \text{from prev. page.}$$

$$= -\frac{\Delta_{\text{vap}}H}{RT^2} = \frac{d}{dT} (\ln x_A)$$

ASSUME:

$\rightarrow \Delta_{\text{vap}}H^\circ$ const. over small ΔT

$\rightarrow T^* =$ normal bp for pure substance, $x_A = 1$

so: $d(\ln x_A) = -\frac{\Delta_{\text{vap}}H}{RT^2} dT$

$$\int_1^{x_A} d(\ln x_A) = -\frac{\Delta_{\text{vap}}H}{R} \int_{T^*}^T \frac{1}{T^2} dT$$

$$\ln x_A = -\frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T} - \frac{1}{T^*}\right) = -\frac{\Delta_{\text{vap}}H}{R} \left(\frac{T-T^*}{TT^*}\right)$$

\Rightarrow for small ΔT , $\Delta T = T - T^*$, $TT^* \approx (T^*)^2$

so: $\ln x_A = -\frac{\Delta_{\text{vap}}H \Delta T}{R(T^*)^2}$

express in terms of SOLUTE, B:

$$\ln(1-x_B) = -\frac{\Delta_{\text{vap}}H \Delta T}{R(T^*)^2}$$

if $x_B \ll 1$, $\ln(1-x_B) \approx -x_B$

therefore: $\Delta T = \frac{R(T^*)^2}{\Delta_{\text{vap}}H} \cdot x_B$

Γ ASIDE:

$$b = \frac{n_B}{n_A M_A} \approx \frac{n_B}{(n_A + n_B) M_A} = \frac{n_B}{n M_A} = \frac{x_B}{M_A}$$

$\underbrace{\hspace{10em}}_{\text{v. small!}}$

$$\therefore x_B = b M_A \quad \square$$

$$\therefore \Delta T = \frac{M_A R(T^*)^2}{\Delta_{\text{vap}}H} \cdot b \quad \text{q.e.d.}$$

$\underbrace{\hspace{10em}}_{K_b}$

(L17) Osmometry and the Van't Hoff Equ'n

$$\Pi = [B]RT$$

osmotic pressure \leftarrow \leftarrow conc. of solute, B

This can be rewritten in a virial form:

$$\Pi = [B]RT \{ \underbrace{1 + B[B]}_{\text{truncate after this...}} + C[B]^2 + \dots \}$$

If $[B] = \frac{c}{M}$, $c = \text{mass conc. (g L}^{-1}\text{)}$, $M = \text{molar mass (g mol}^{-1}\text{)}$

and Π is related to HYDROSTATIC PRESSURE:

$$\Pi = \rho g h$$

Then: $\rho g h = \frac{c}{M} RT \left\{ 1 + \frac{Bc}{M} \right\}$

Rearrange such that $\frac{h}{c}$ is on LHS:

$$\frac{h}{c} = \frac{RT}{\rho g M} \left\{ 1 + \frac{Bc}{M} \right\}$$

$$\frac{h}{c} = \underbrace{\frac{RT}{\rho g M}}_{b \text{ (intercept)}} + \underbrace{\frac{RTB}{\rho g M^2}}_a \cdot c \quad \text{i.e., } y = ax + b$$

(slope)

\therefore A plot of $\frac{h}{c}$ vs. c allows for the determination of molecular mass, M