Colligative Properties (1)

Non-volatile solute B in volatile solvent A.

If ideal, $p_A = X_{A.\ell}\, p_A^*$

1) Vapor pressure lowering:

$\Delta p_A = p_A^* - p_A = p_A^* - X_{A.\ell}\, p_A^* = (1 - X_{A.\ell}) p_A^*$

$\Delta p_A = X_{B.\ell}\, p_A^*$

The lowering of the equilibrium vapor pressure of the solution is proportional to the concentration of solute B.

The proportionality constant is a property of A, the identity of B plays no role.

Colligative Properties (2)

Non-volatile solute B in volatile solvent A.

2) Boiling point elevation

From general chemistry: $\mathbf{\Delta T_{bp} \equiv T_{bp} - T_{bp}^* = K_b\, m}$

The elevation of the boiling point of the solution is proportional to the concentration of solute B.

The proportionality constant is a property of A; the identity of B plays no role.

Where does this come from?

slide 26: $\mu_{A,\ell} = \mu_{A,\ell}^* + RT \ln X_{A,\ell}$

Gas is pure A, so at T_{bp}, $\mu_{A,g}^* = \mu_{A,\ell}$

Colligative Properties (3)

$\mu_{A,g}^* = \mu_{A,\ell}^* + RT \ln X_{A,\ell}$

$RT \ln X_{A,\ell} = \mu_{A,g}^* - \mu_{A,\ell}^* = \Delta_{vap}G°$ (at one atm.)

$R \ln X_{A,\ell} = \Delta_{vap}G°/T$

take d/dT of both sides, using Gibbs-Helmholtz:

$R\, d \ln X_{A,\ell} /dT = d(\Delta_{vap}G°/T)/dT = -\Delta_{vap}H°/T^2$

$d \ln X_{A,\ell} = (-\Delta_{vap}H°/RT^2)\, dT$

Integrate from (X_A=1, $T = T_{bp}^*$) to (X_A, T_{bp}):

assuming that $\Delta_{vap}H°$ is constant

$\ln X_{A,\ell} = (+\Delta_{vap}H°/R)(1/T_{bp} - 1/T_{bp}^*)$

but $\ln X_{A,\ell} = \ln(1 - X_{B,\ell})$, so

Colligative Properties (4)

$\ln(1 - X_{B,\ell}) = (\Delta_{vap}H°/R)(1/T_{bp} - 1/T_{bp}^*)$

When x is small, ln (1–x) = –x, so

$X_{B,\ell} = -(\Delta_{vap}H°/R)(1/T_{bp} - 1/T_{bp}^*)$

$= -(\Delta_{vap}H°/R)([T_{bp}^* - T_{bp}] / T_{bp} T_{bp}^*)$

$X_{B,\ell} = \Delta T_{bp}\, (\Delta_{vap}H°/ R T_{bp} T_{bp}^*)$

Make the approximation that $T_{bp} T_{bp}^* = T_{bp}^{*2}$

$X_{B,\ell} = \Delta T_{bp}\, (\Delta_{vap}H°/R T_{bp}^{*2})$

$\Delta T_{bp} = X_{B,\ell}\, (R T_b^{*2}/\Delta_{vap}H°)$

$X_B = m / (m + 1000/M_A) \approx m M_A/1000$

$\Delta T_{bp} = (M_A R T_b^{*2}/ 1000 \Delta_{vap}H°)\, m$ $\mathbf{= K_b\, m}$