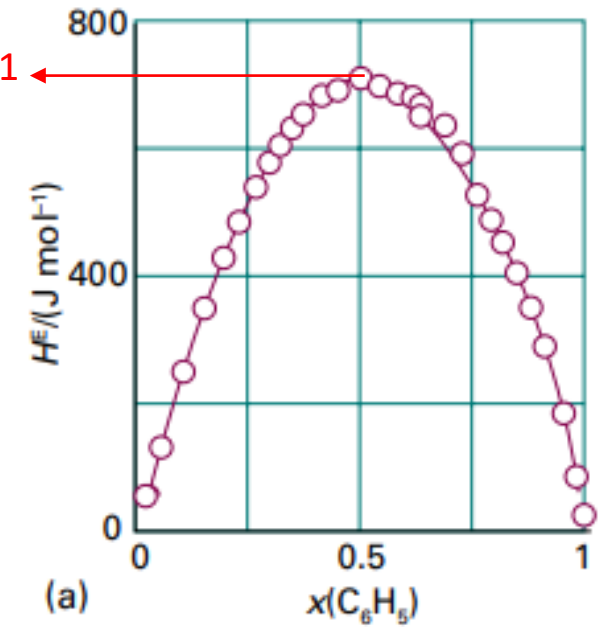


Regular solutions

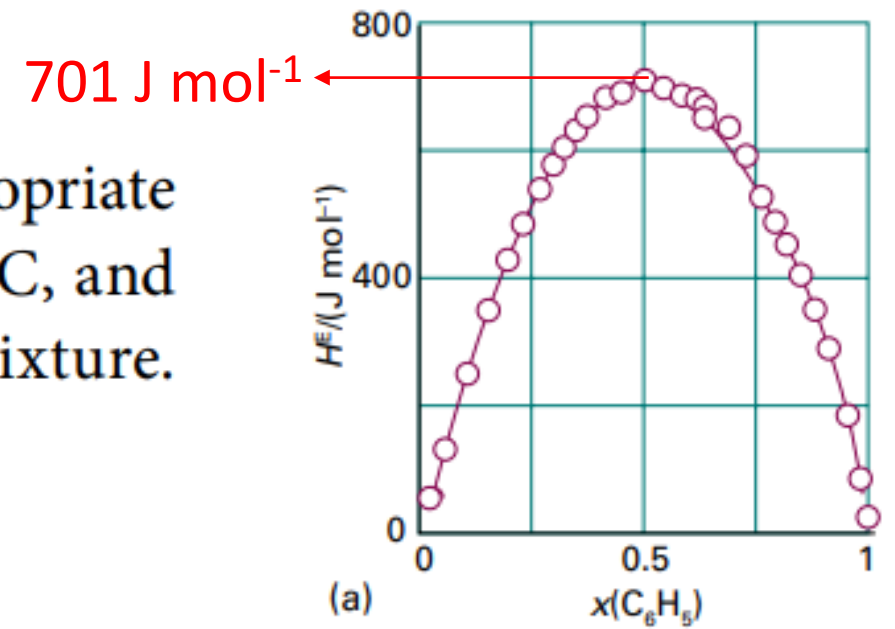
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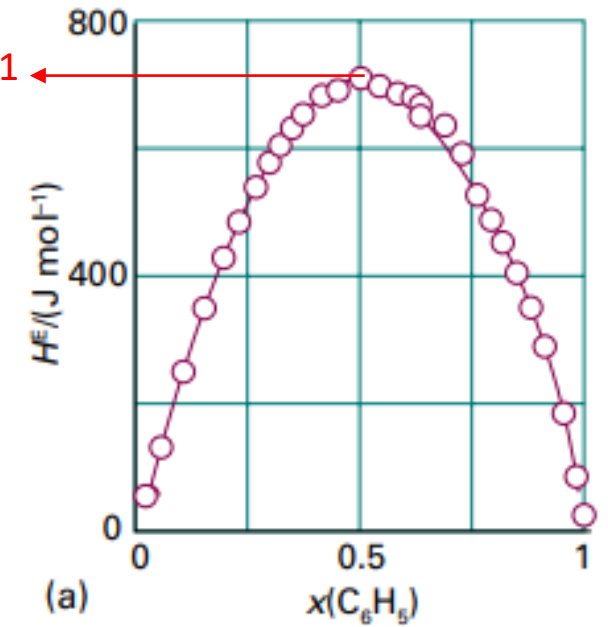
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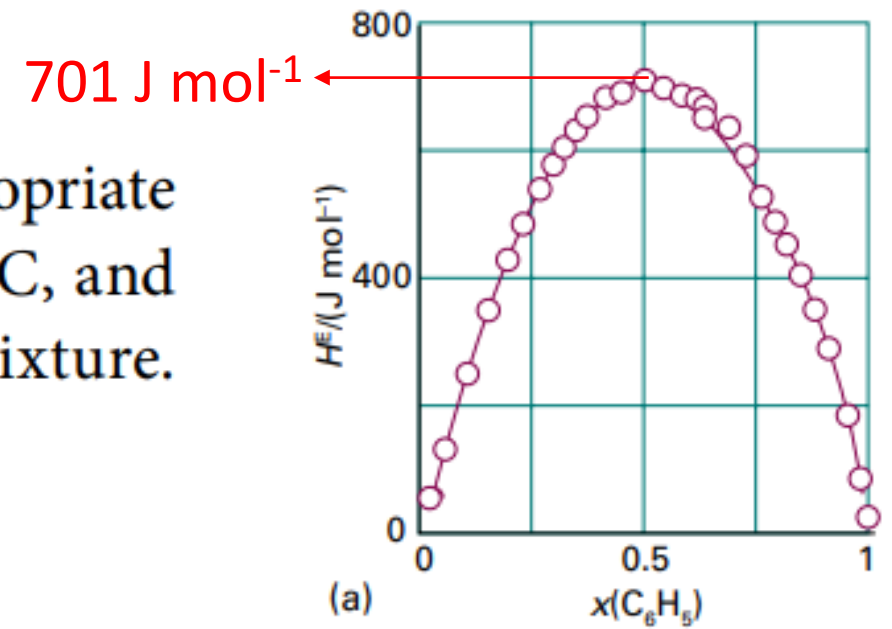
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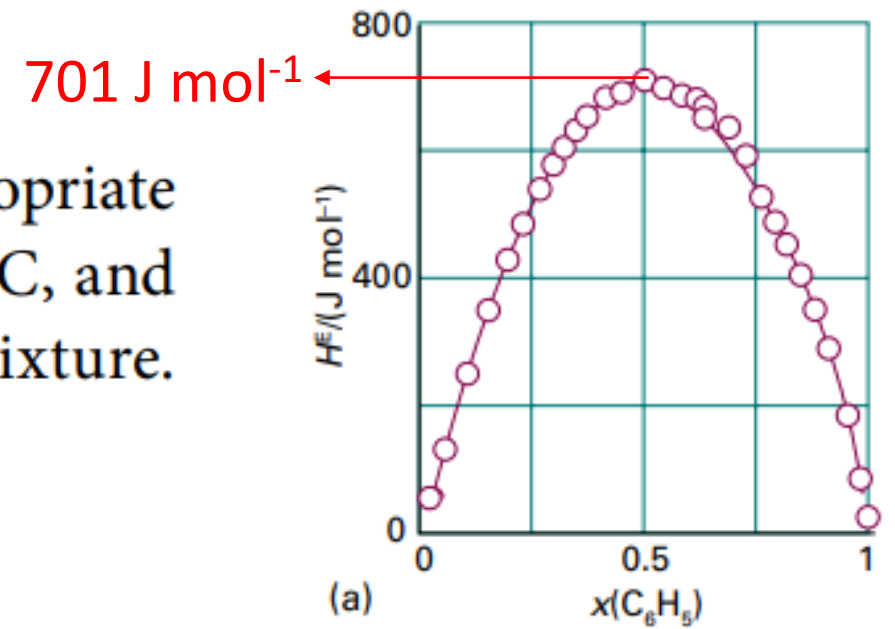


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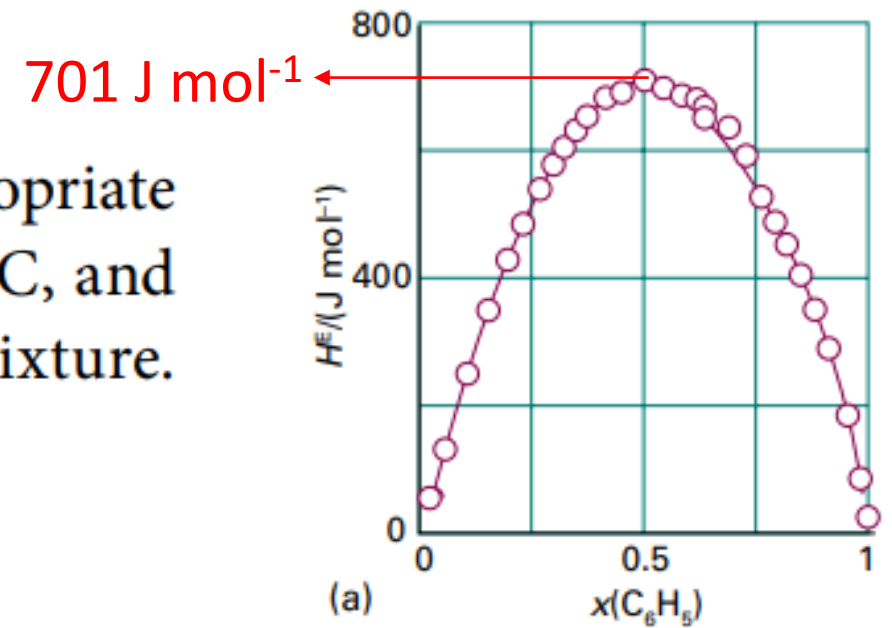
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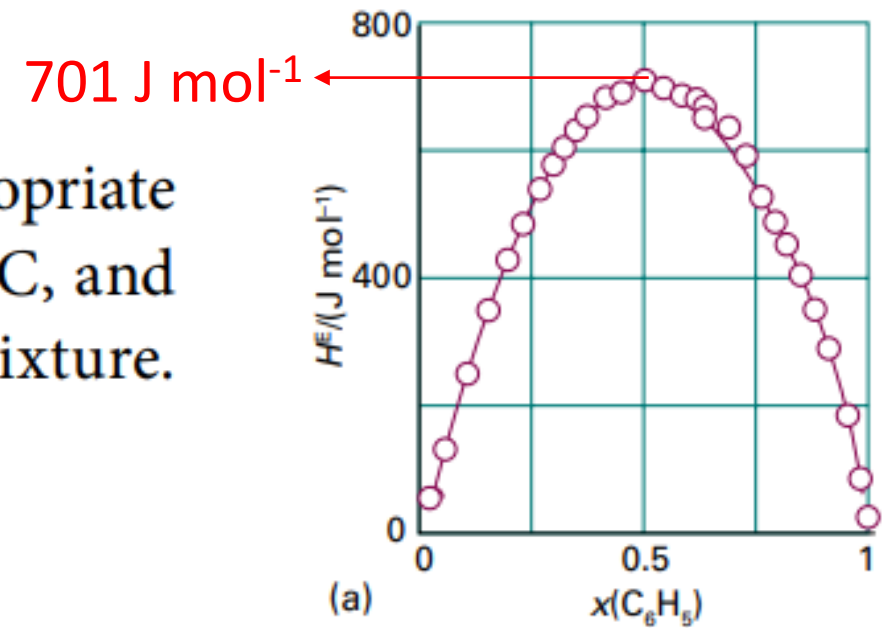
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Colligative properties

..depends on the relative number of solute particles present but not their chemical identity

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- vapor pressure lowering
- boiling point elevation
- freezing point depression
- osmotic pressure

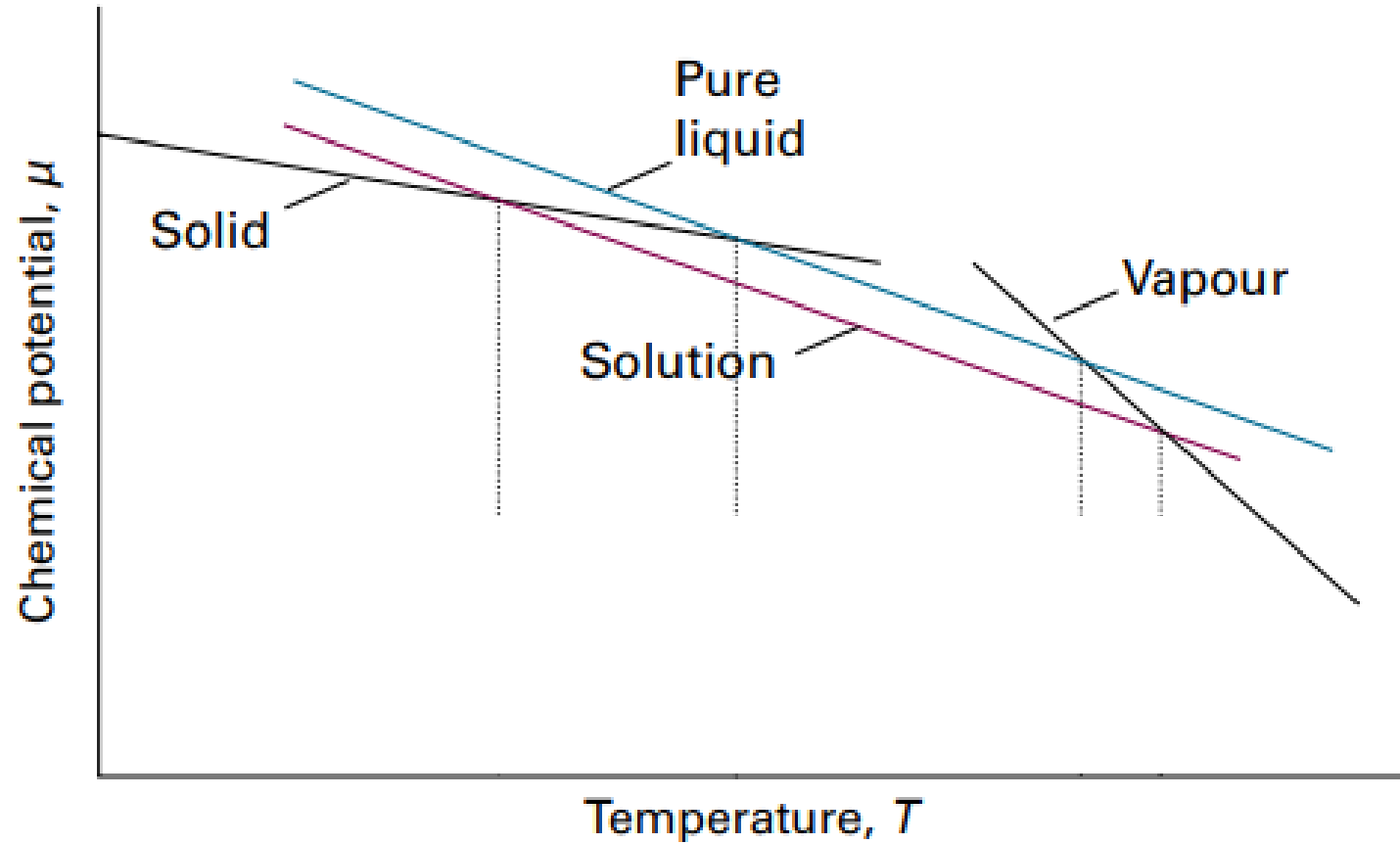
FP depression and BP elevation

FP depression and BP elevation

pure $\mu_A = \mu_A^*$

with solute B $\mu_A = \mu_A^* + RT \ln x_A$

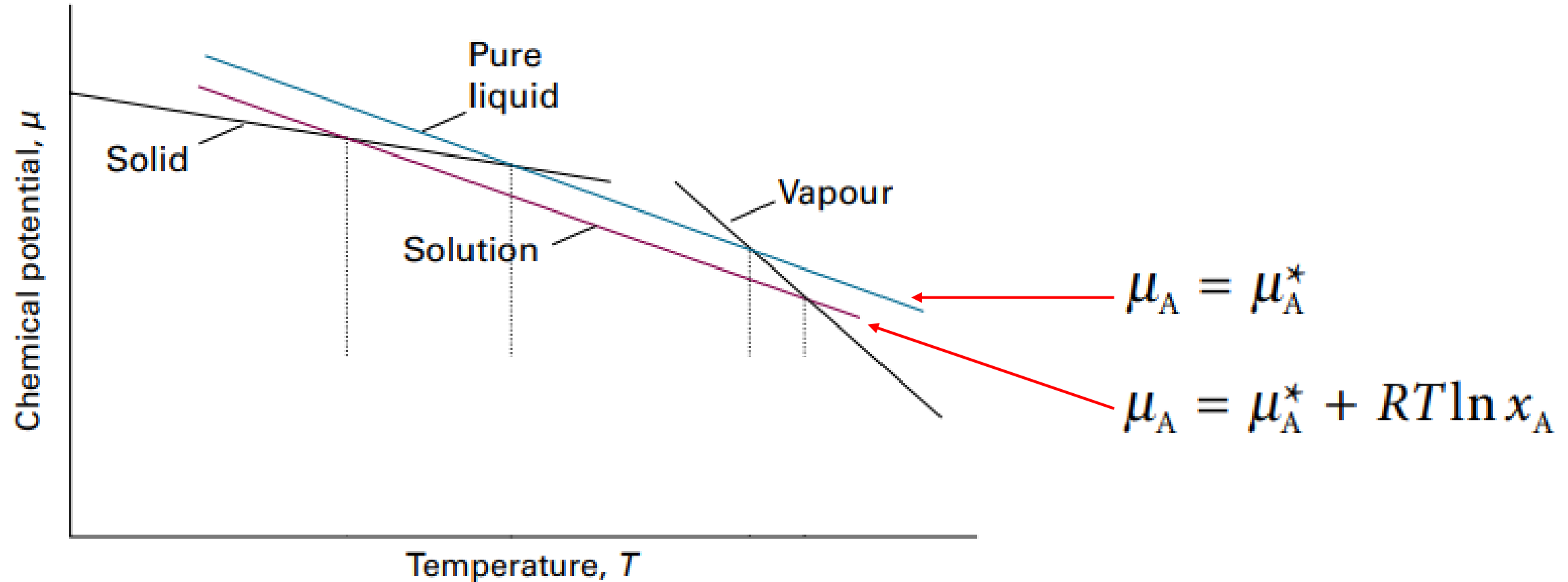
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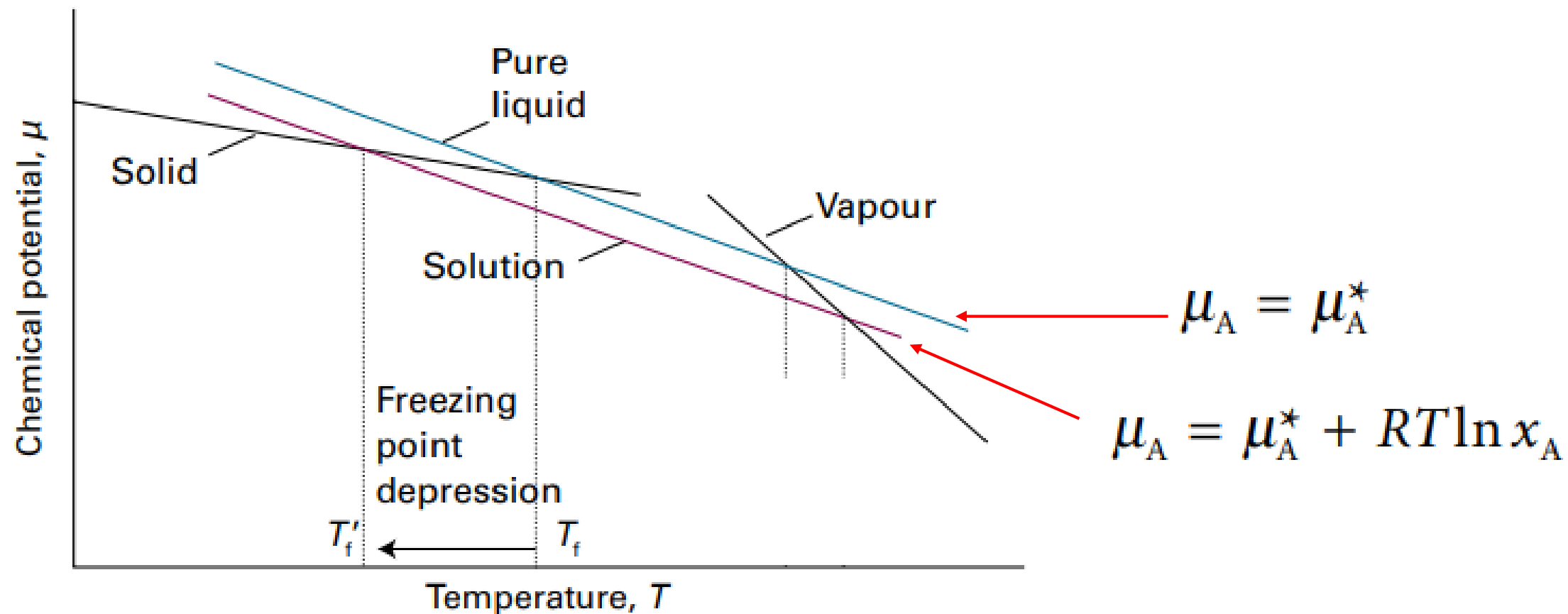
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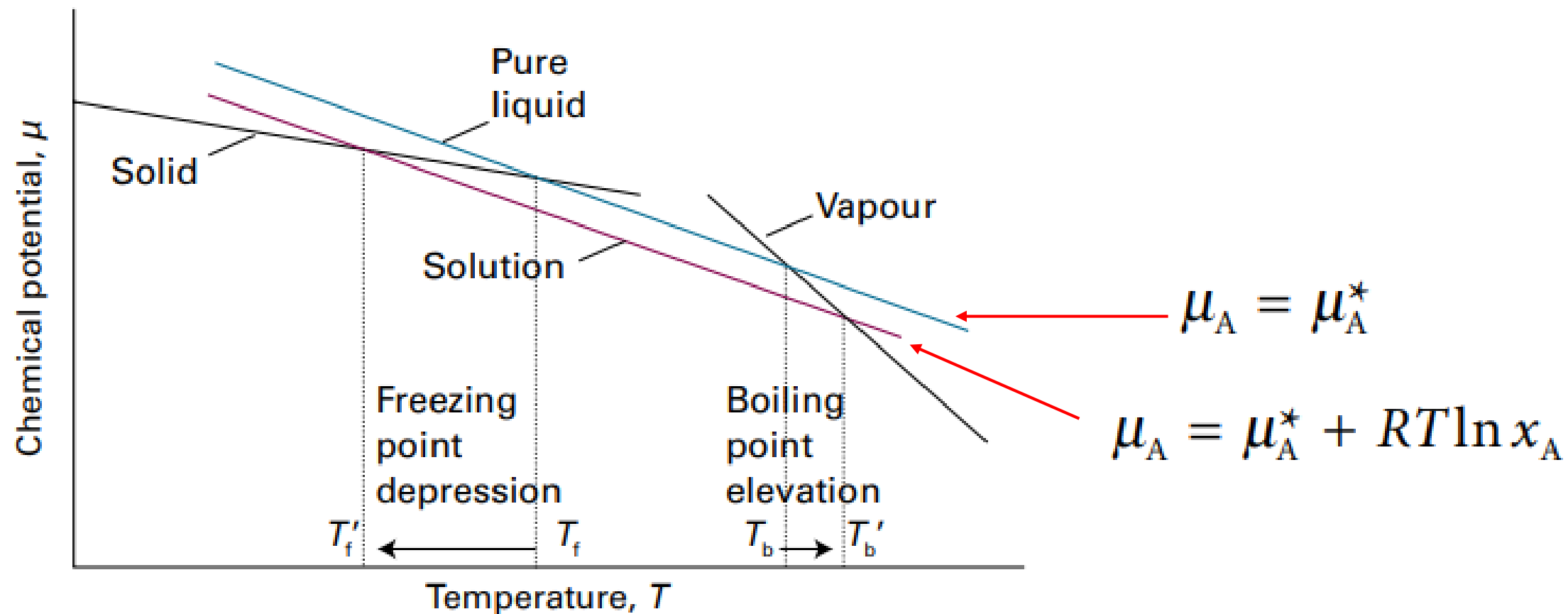
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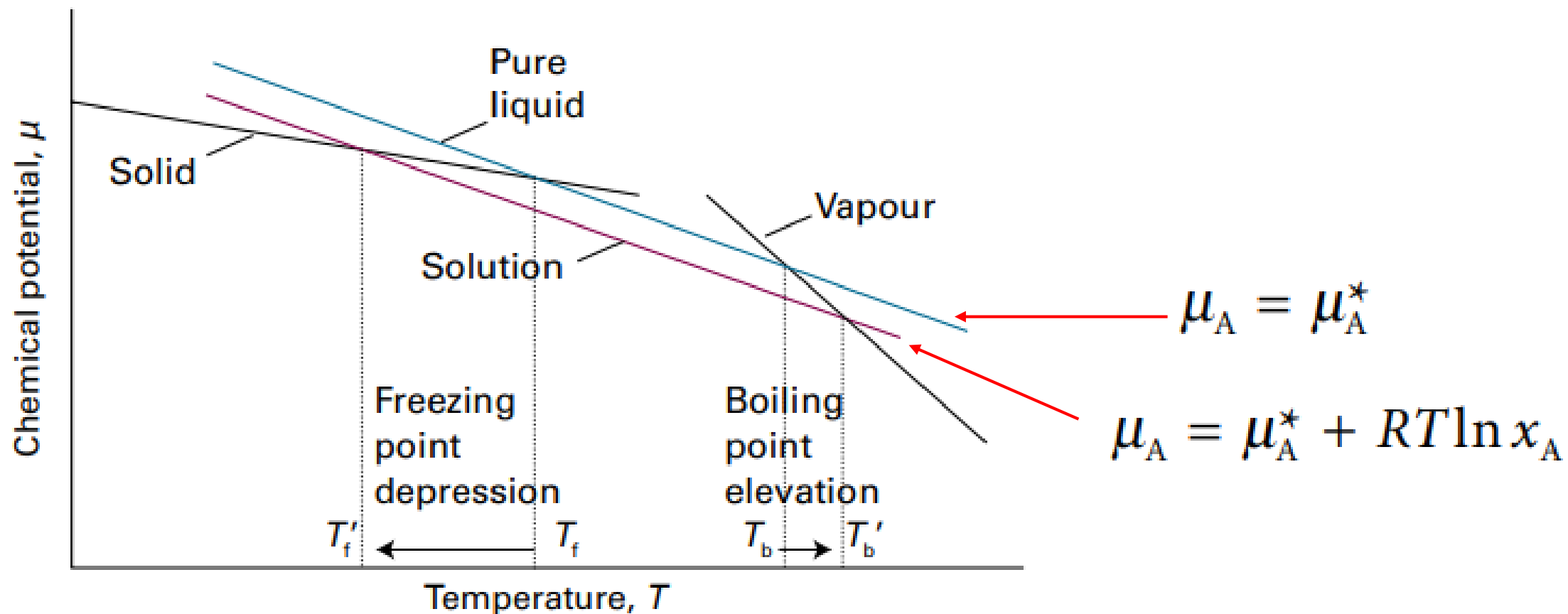


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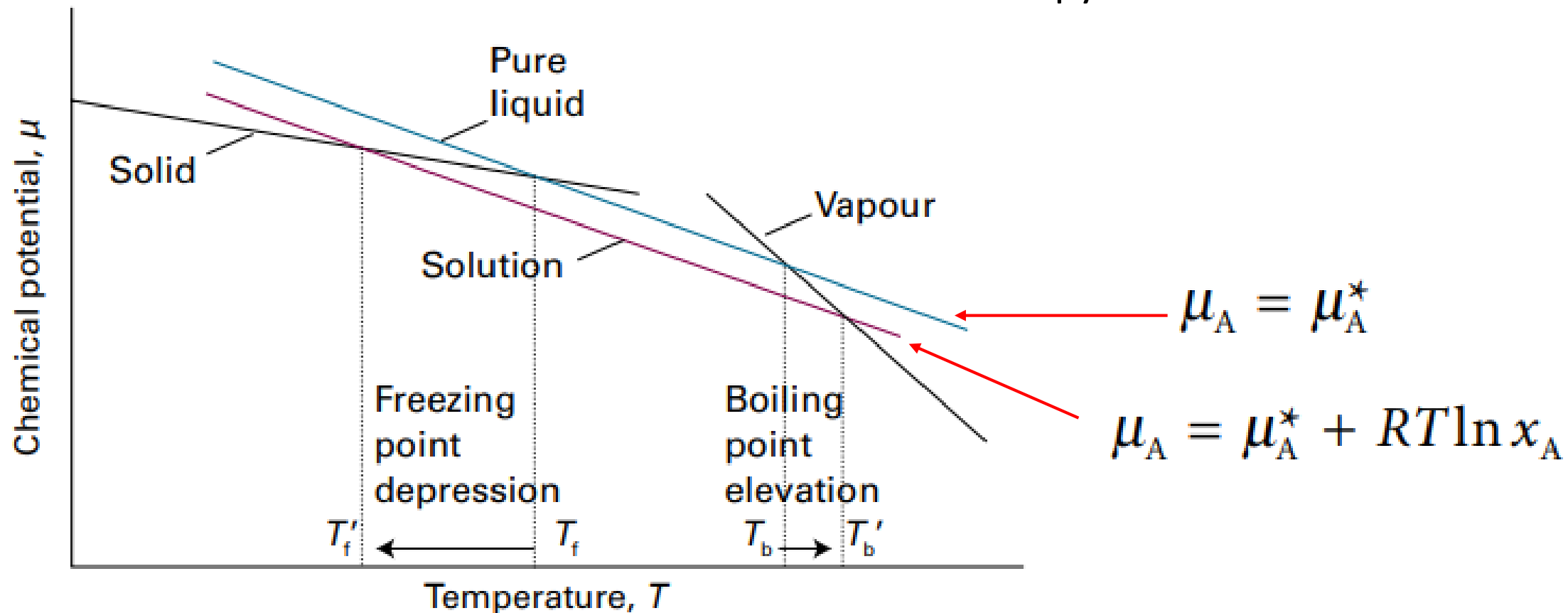
This occurs even in ideal solutions



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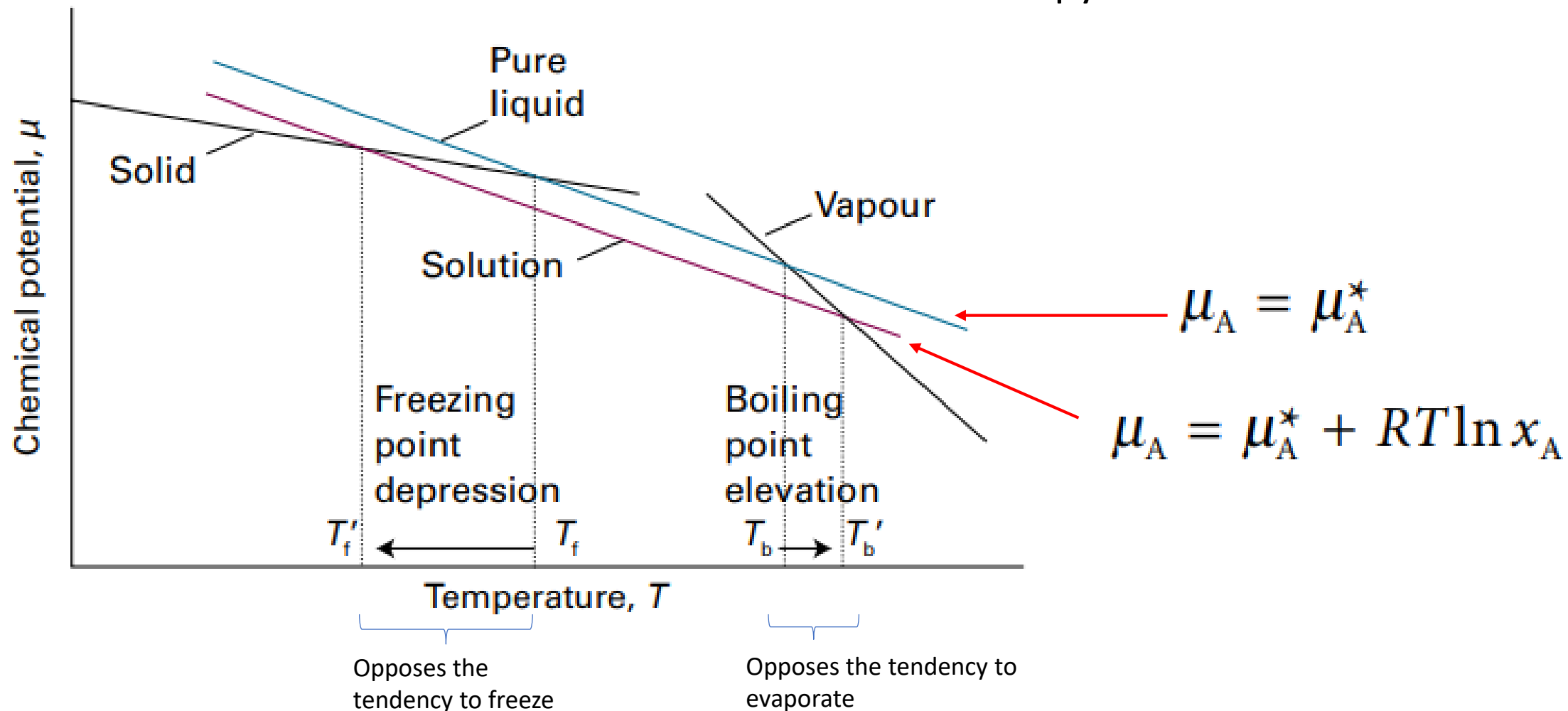
An entropy effect!



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Solute: An additional contribution to the entropy => weaker tendency to form the vapor => raises the boiling point

FP depression and BP elevation

This occurs even in ideal solutions

An entropy effect!

Solute: An additional contribution to the entropy => weaker tendency to form the vapor => raises the boiling point

Solute: An enhanced molecular randomness in solution => opposes the tendency to freeze => requires lower temperature => lowers the FP

Elevation of BP

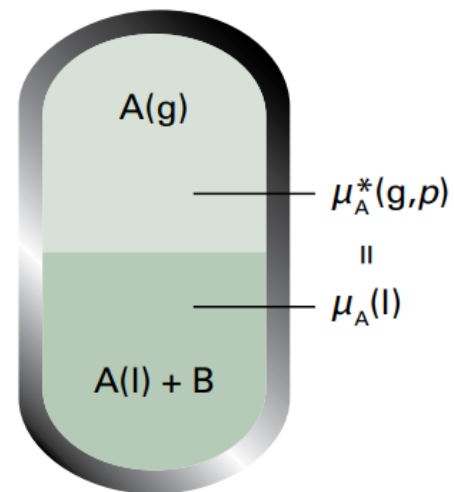
The elevation in boiling point (ΔT) is directly proportional to the molality of the solute (m_B)

Elevation of BP

$$\mu_A = \mu_A^* + RT \ln x_A$$

Elevation of BP

$$\mu_A = \mu_A^* + RT \ln x_A$$



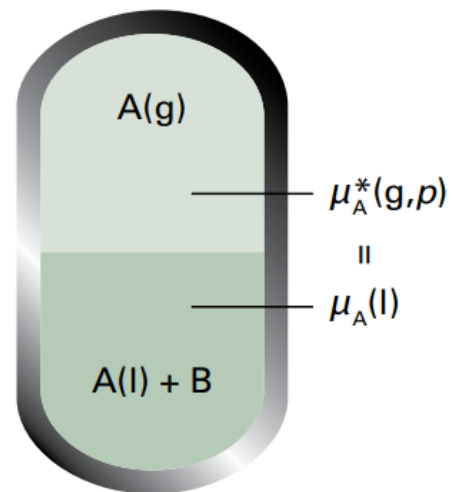
At the BP

Assume B is non-volatile

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At the BP

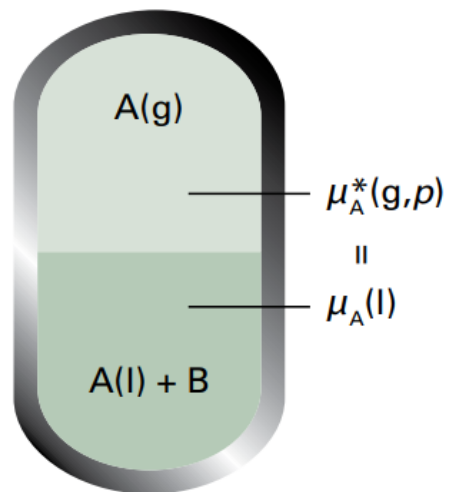
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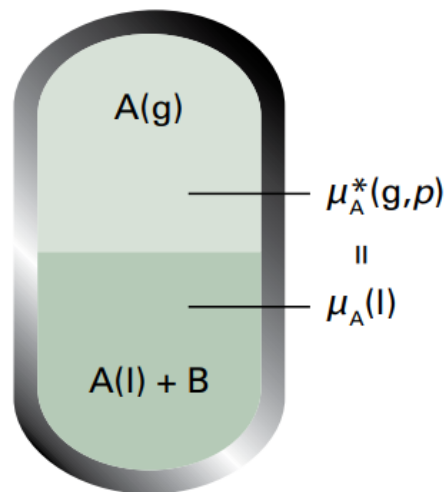


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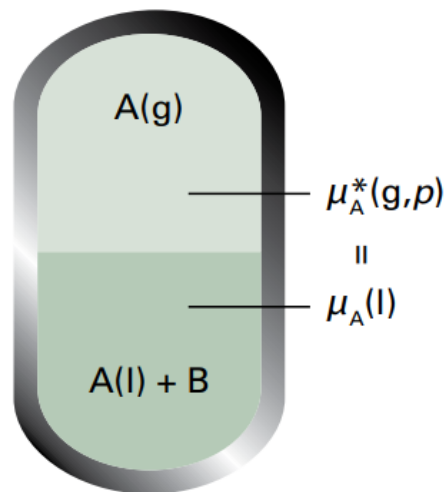
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Variation with T:

$$\frac{d \ln x_A}{dT} = \frac{1}{R} \frac{d(\Delta_{\text{vap}} G/T)}{dT}$$



Elevation of BP

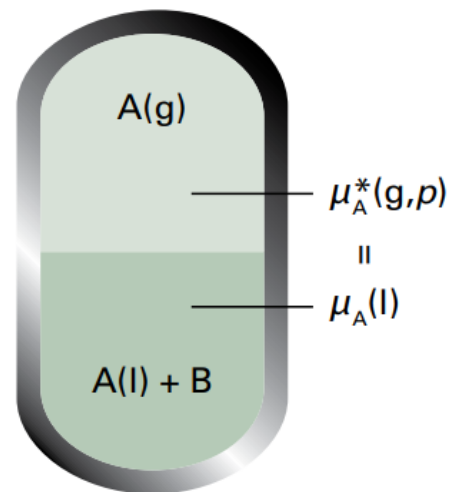
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$$\left| \left(\frac{\partial G/T}{\partial T} \right)_p = -\frac{H}{T^2} \right| \quad (3E.10)$$

Gibbs-Helmholtz equation

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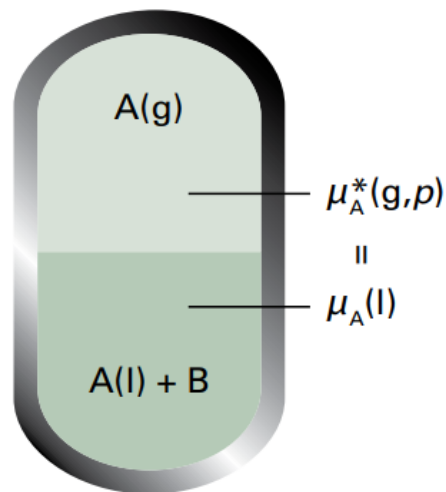
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Enthalpy of vaporization is assumed to be constant over the small range of temperature

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Elevation of BP

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Elevation of BP

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Suppose, $x_B \ll 1$; the approximation $\ln(1-x) \approx -x$

The Taylor series for $\ln(1-x)$ around $x=0$ is:

$$\ln(1-x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \frac{x^4}{4} - \dots$$

So if x is **small**, then:

- $x^2, x^3, \dots$ are **even smaller**, and can be neglected.
- That means:

$$\ln(1-x) \approx -x$$

Elevation of BP

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

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increase in the boiling point is small

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$$x_B = \frac{\Delta_{\text{vap}}H}{R} \times \frac{\Delta T_b}{T^{*2}}$$

$$\Delta T_b = K x_B \quad K = \frac{RT^{*2}}{\Delta_{\text{vap}}H}$$

Elevation of BP

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$$b = \frac{\text{mol}}{\text{kg}}$$

b = molality

mol = moles of solute

kg = kilogram of solvent

When the solution is dilute, the mole fraction of solute is approximately proportional to molality:

$$x_B = \frac{n_B}{n_A + n_B}$$

$$\text{If } n_B \ll n_A, \text{ then } x_B \approx \frac{n_B}{n_A}$$

$$m = \frac{n_B}{M_A \cdot n_A}$$

$$\frac{n_B}{n_A} = m \cdot M_A$$

$$x_B \approx m \cdot M_A$$

Elevation of BP

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empirical boiling-point constant

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$x_B \ll 1$, x_B is proportional to its molality, b

$$\Delta T_b = K_b b$$

No reference to the identity of the solute;
thus, a colligative property!

Elevation of BP

$$\Delta T_b = K_b b$$



$$K = \frac{RT^{\star 2}}{\Delta_{\text{vap}} H}$$

empirical boiling-point constant

The change in bp depends on the solvent.

Elevation of BP

$$\Delta T_b = K_b b$$



$$K = \frac{RT^{*2}}{\Delta_{\text{vap}} H}$$

The change in bp depends on the solvent.

empirical boiling-point constant

	$K_f/(\text{K kg mol}^{-1})$	$K_b/(\text{K kg mol}^{-1})$
Benzene	5.12	2.53
Camphor	40	
Phenol	7.27	3.04
Water	1.86	0.51

Elevation of BP

$$\Delta T_b = K_b b$$



empirical boiling-point constant

	$K_f/(\text{K kg mol}^{-1})$	$K_b/(\text{K kg mol}^{-1})$
Benzene	5.12	2.53
Camphor	40	
Phenol	7.27	3.04
Water	1.86	0.51

What is the elevation of the BP of

- 1) Water
- 2) Benzene

When a solute is present at a molality of 0.10 mol kg^{-1}

Elevation of BP

$$\Delta T_b = K_b b$$



empirical boiling-point constant

	$K_f/(\text{K kg mol}^{-1})$	$K_b/(\text{K kg mol}^{-1})$
Benzene	5.12	2.53
Camphor	40	
Phenol	7.27	3.04
Water	1.86	0.51

What is the elevation of the BP of

- 1) Water **0.051 K**
- 2) Benzene **0.25 K**

When a solute is present at a molality of 0.10 mol kg^{-1}

Depression of Freezing Point

$$\mu_A^*(s) = \mu_A^*(l) + RT \ln x_A$$

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BP elevation

$$\mu_A^*(g) = \mu_A^*(l) + RT \ln x_A$$

Depression of Freezing Point

$$\mu_A^*(s) = \mu_A^*(l) + RT \ln x_A$$

BP elevation

$$\mu_A^*(g) = \mu_A^*(l) + RT \ln x_A$$

$$\Delta T_b = K x_B \quad K = \frac{RT^{\star 2}}{\Delta_{\text{vap}} H}$$

Depression of Freezing Point

$$\mu_A^*(s) = \mu_A^*(l) + RT \ln x_A$$

$$\Delta T_f = K' x_B \quad K' = \frac{RT^{*2}}{\Delta_{\text{fus}} H}$$

BP elevation

$$\mu_A^*(g) = \mu_A^*(l) + RT \ln x_A$$

$$\Delta T_b = K x_B \quad K = \frac{RT^{*2}}{\Delta_{\text{vap}} H}$$

Depression of Freezing Point

$$\mu_A^*(s) = \mu_A^*(l) + RT \ln x_A$$

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$$\Delta T_b = K x_B \quad K = \frac{RT^{*2}}{\Delta_{\text{vap}} H}$$

T^* is the freezing point of the pure liquid

$\Delta_{\text{fus}} H$ is the enthalpy of fusion of the solvent

Depression of Freezing Point

$$\mu_A^*(s) = \mu_A^*(l) + RT \ln x_A$$

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T^* is the freezing point of the pure liquid

$\Delta_{\text{fus}} H$ is the enthalpy of fusion of the solvent

When the solution is dilute,

$$\Delta T_f = K_f b$$

K_f is the empirical freezing-point constant
 b is the molality of the solute

Depression of Freezing Point

$$\Delta T_f = K_f b$$

	$K_f/(\text{K kg mol}^{-1})$	$K_b/(\text{K kg mol}^{-1})$
Benzene	5.12	2.53
Camphor	40	
Phenol	7.27	3.04
Water	1.86	0.51

What is the depression of the FP of

1) Water

2) Benzene

When a solute is present at a molality of 0.10 mol kg^{-1}

Depression of Freezing Point

$$\Delta T_f = K_f b$$

	$K_f/(\text{K kg mol}^{-1})$	$K_b/(\text{K kg mol}^{-1})$
Benzene	5.12	2.53
Camphor	40	
Phenol	7.27	3.04
Water	1.86	0.51

What is the depression of the FP of

1) Water **0.186 K**

2) Benzene **0.51 K**

When a solute is present at a molality of 0.10 mol kg^{-1}

Depression of Freezing Point

$$\Delta T_f = K_f b$$

	$K_f/(\text{K kg mol}^{-1})$	$K_b/(\text{K kg mol}^{-1})$
Benzene	5.12	2.53
Camphor	40	
Phenol	7.27	3.04
Water	1.86	0.51

What is the depression of the FP of

1) Water **0.186 K**

2) Benzene **0.51 K**

BP
0.051 K
0.25 K

When a solute is present at a molality of 0.10 mol kg^{-1}

Freezing requires precise molecular ordering (forming a solid lattice), which is more easily disrupted by solute particles than the process of molecules escaping to vapor.