7. Solutions

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In all discussions of mixtures we will be using the concept that <u>at equilibrium</u> the <u>chemical potential of a substance must be the same throughout</u> the sample, regardless of how many phases are present.

Suppose we have liquid and vapor phases and one component, then pure liquid and its vapor:

❀ $\mu_{\text{vap}}(T,p) = \mu_{\text{liquid}}(T,p)$

$\mu_{\text{vapor}}(T,p)$ = one of the following:

$$\mu_{\text{id}}(T) = \mu^{\ominus}_{T} + RT \ln \frac{p}{1} \qquad \text{(ideal gas)}$$

$$\mu(T) = \mu^{\ominus}_{T} + RT \ln \frac{f}{1} \qquad \text{(real gas)}$$

7.1 The Ideal Solution, Raoult's law

Suppose we have liquid and vapor phases and two components, solvent A and solute B, then

solution and its vapor:

❀ $\mu_{\mathrm{A,\,liquid}} = \mu_{\mathrm{A,vap}}$

$\mu_{\mathrm{A,vap}} = \mu^{\ominus}_{T} + RT\ln(p_A/1)$ (ideal)

pure liquid and its vapor, use * to denote values for pure substance:

❀ $\mu^*_{\mathrm{A,\,liquid}} = \mu^*_{\mathrm{A,vap}}$

$\mu^*_{\mathrm{A,vap}} = \mu^{\ominus}_{T} + RT\ln(p^*_A/1)$ (ideal vapor)

Subtract:

$\mu_{\mathrm{A,\,liquid}} - \mu^*_{\mathrm{A,\,liquid}} = RT\ln(p_A/p^*_A)$ (ideal vapor)

$\mu_{\mathrm{A,\,liquid}} - \mu^*_{\mathrm{A,\,liquid}} = RT\ln(f_A/f^*_A)$ (real vapor)

Raoult discovered experimentally the limiting behavior for solutions made up of mostly solvent A, the relation between *p* the vapor pressure of A over a solution containing A and p^*_A the vapor pressure of A over pure liquid.

$p/p^*_A = x_A$ **Raoult's law**

Define: a solution that obeys Raoult's law for all concentrations is an ***ideal solution*** (the vapor does not have to behave as an ideal gas):

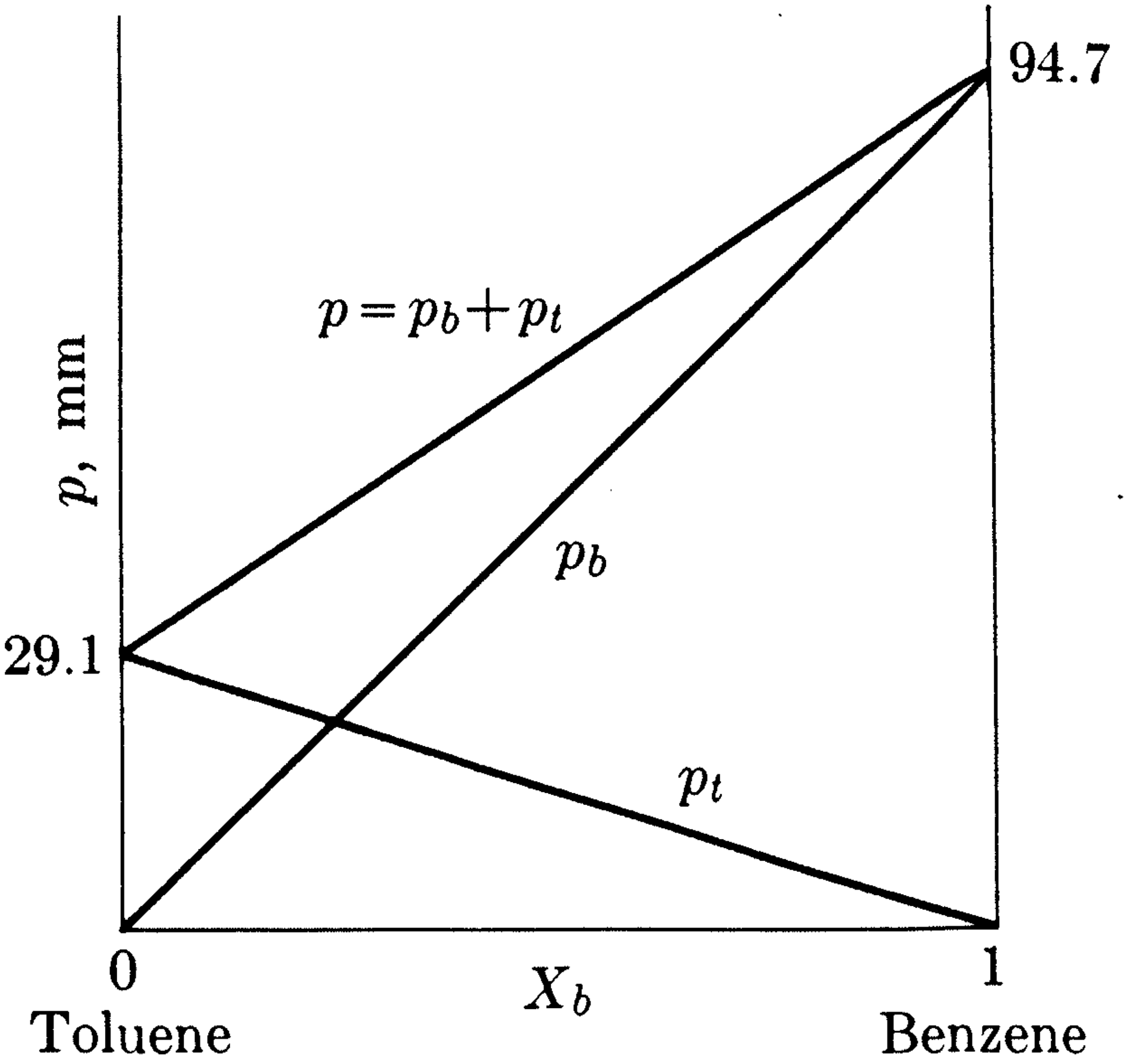
For ideal solutions

$\mu_{A,\text{ liquid}} - \mu^*_{A,\text{ liquid}} = RT\ln x_A$ (***ideal solution***)

$\mu_{A,\text{ liquid}}$ is the chemical potential of the solvent in the liquid solution

$\mu^*_{A,\text{ liquid}}$ is the chemical potential of the pure liquid solvent

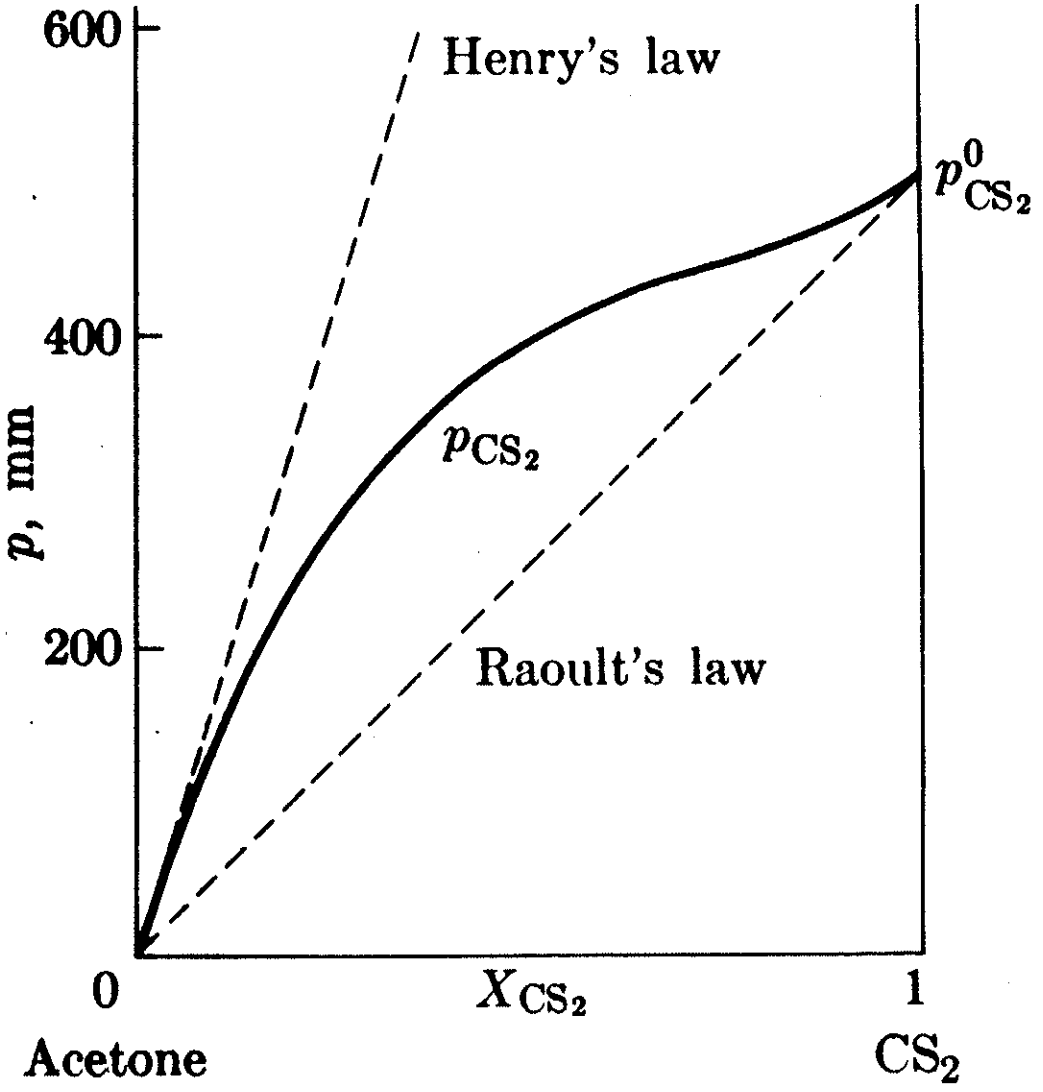
x_A is the mole fraction of solvent in the liquid solution.



If, in addition, the vapor behaves ideally, then the mole fraction of A in the vapor phase, y_A, is, according to partial pressures in the vapor: $y_A = p_A/(p_A+p_B)$

Near $x_A = 1$, $p_A = p^*_A x_A$ Raoult's law

Near $x_A = 0$, $p_A = K_{H,A} x_A$ Henry's Law



7.2 The Gibbs-Duhem Equation

In general, when the number of moles can change (open system), i.e., $dn \neq 0$
$d\boldsymbol{G} = V dp - \boldsymbol{S} dT + \mu_A \, dn_A + \mu_B \, dn_B$

at constant T and p,
$d\boldsymbol{G}_{T,p} = \mu_A \, dn_A + \mu_B \, dn_B$

Since μ_A is the Gibbs free energy per mole of A, for a two-component mixture,
$\boldsymbol{G} = n_A \mu_A + n_B \mu_B$
When the composition is changed infinitesimally, mathematically we can write
$d\boldsymbol{G} = \mu_A \, dn_A + n_A \, d\mu_A + \mu_B dn_B + n_B \, d\mu_B$

Comparing the two we must therefore have, $n_A \, d\mu_A + n_B \, d\mu_B = 0$

or more generally, for more than 2 components,

$\boxed{\sum_i n_i \, d\mu_i = 0 \qquad \textbf{\textit{Gibbs-Duhem eqn.}}}$

That is, the chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components.

7.3 The Chemical Potential in the Ideal Dilute Solution

The Gibbs-Duhem equation can be used to calculate the chemical potential of the solute from that of the solvent ina binary ideal solution:

Start with:

$n_A \, d\mu_A + n_B \, d\mu_B = 0$ Gibbs-Duhem eqn.

$d\mu_B = -(n_A / n_B) \, d\mu_A = -(x_A / x_B) \, d\mu_A$

Now specialize to an ideal solution:

For ideal solutions

$\mu_{\text{A, liquid}} - \mu^*_{\text{A, liquid}} = RT\ln x_A$ (ideal solution)

Keeping T and p constant, differentiate,

$d\mu_{\text{A, liquid}} = RT d\ln x_A = RT(dx_A / x_A)$

But Gibbs-Duhem had

$d\mu_B = -(x_A / x_B)\, d\mu_A$

Replace $d\mu_A$ in above, to get

$d\mu_B = -(x_A/x_B)RT(dx_A/x_A) = -(RT/x_B)dx_A$

Now use

$x_A + x_B = 1$, $dx_A + dx_B = 0$ or $dx_A = -dx_B$

we get

$$\boxed{d\mu_B = (RT/x_B)dx_B}$$

For component B

$\mu_{\text{B, liquid}} - \mu^*_{\text{B, liquid}} = RT\ln x_B$ (ideal solution)

is consistent with the above eqn. box.

7.4 Henry's law

Another experimental finding is that in the limiting case of a solution very dilute in the solute B, the partial pressure of B in the vapor is directly proportional to the mole fraction of B in the liquid:

$$\boxed{p_B = K_H x_B \qquad \textbf{\textit{Henry's law}}}$$

This equation also says:
The equilibrium molefraction x_B, the solubility of a gas in the solution, is related to the partial pressure of that constituent in the gaseous phase in equilibrium with the liquid.

7.5 Colligative Properties, Freezing Point Depression, Boiling Point Elevation, Osmotic Pressure

We now consider the situation when the <u>solute is non-volatile</u> (does not have a contribution to the vapor pressure).

For a solution in equilibrium with the vapor of the pure solvent

❀ $\mu_{A,\text{ liquid}}\ (T,p,x_A) = \mu_{A,\text{vap}}\,(T,p)$

If the solution is ideal, then

$\mu_{A,\text{liquid}} - \mu^*_{A,\text{liquid}} = RT\ln x_A$ (ideal solution)

or more explicitly,

$\mu_{A,\text{liquid}}(T,p,x_A) = \mu^*_{A,\text{liquid}}\,(T,p) + RT\ln x_A$

Thus,

$$\mu^*_{A,\text{liquid}}\,(T,p) + RT\ln x_A = \mu_{A,\text{vap}}\,(T,p)$$

$$\begin{aligned}\ln x_A &= [\mu_{A,\text{vap}}\,(T,p) - \mu^*_{A,\text{liquid}}]\,/RT \\ &= \Delta_{vap}\mathbf{G}/RT\end{aligned}$$

Now for the boiling point:

To discover how T depends on x_A, p being constant, we need to evaluate $(\partial T/\partial x_A)_p$.

Differentiate this eq. ↓ with respect to x_A

$$\ln x_A = (1/R)\,(\Delta_{vap}\boldsymbol{G}/T)$$

$$d\ln x_A/dx_A = (1/R)[\partial(\Delta_{vap}\boldsymbol{G}/T)\partial T]_p(\partial T/\partial x_A)_p$$

$$(1/x_A) = -\,(1/R)[\,\Delta_{vap}\boldsymbol{H}/T^2]_p(\partial T/\partial x_A)_p \;.$$

Now integrate between

pure solvent ($x_A = 1$ and $T = T^*$)

and solution (x_A and T):

$$\int_1^{xA} dx_A/x_A = -\,(1/R)\int_{T^*}^{T} [\Delta_{vap}\boldsymbol{H}/T^2]\;dT$$

If further, $\Delta_{vap}\boldsymbol{H}$ is nearly independent of temperature,

$$\boxed{\ln x_A = \Delta_{vap}\boldsymbol{H}/R\left[\frac{1}{T} - \frac{1}{T^*}\right]}$$

Since $\ln x_A$ is negative, $T > T^*$.

The boiling point of the solution containing a non-volatile solute is higher than that of the pure solvent.

Now let us consider the freezing point:

For a solution in equilibrium with the solid of the pure solvent

❀ $\mu_{\mathrm{A,liquid}}\ (T,p,x_A) = \mu_{\mathrm{A,solid}}\ (T,p)$

If the solution is ideal, then

$\mu_{\mathrm{A,liquid}} - \mu^{*}_{\mathrm{A,liquid}} = RT \ln x_A$ (ideal
or more explicitly, solution)

$\mu_{\mathrm{A,liquid}}\ (T,p,x_A) = \mu^{*}_{\mathrm{A,liquid}}\ (T,p) + RT \ln x_A$

Thus,

$\mu_{\mathrm{A,solid}}\ (T,p) = \mu^{*}_{\mathrm{A,liquid}}\ (T,p)\ + RT \ln x_A$

$$\ln x_A = [\mu_{\mathrm{A,solid}}\ (T,p) - \mu^{*}_{\mathrm{A,liquid}}\ ]/RT$$
$$= - \Delta_{fus}\,\boldsymbol{G}/RT = - (1/R)(\ \Delta_{fus}\,\boldsymbol{G}/T)$$

Now for the freezing point:

To discover how T depends on x_A,

p being constant,

we need to evaluate $(\partial T/\partial x_A)_{\ p}$

Differentiate with respect to x_A

$$\mathrm{d}\ln x_A/\mathrm{d}x_A = -(1/R)[\partial(\Delta_{fus}\boldsymbol{G}/T)/\partial T]_p(\partial T/\partial x_A)_p$$

$$(1/x_A)\ =\ (1/R)[\ \Delta_{fus}\boldsymbol{H}/T^2]_{\ p}\ (\partial T/\partial x_A)_p$$

Now integrate between

pure solvent ($x_A = 1$ and $T = T^*$)

and solution (x_A and T):

$$\int_1^{xA} dx_A / x_A = (1/R) \int_{T^*}^{T} [\Delta_{fus} \boldsymbol{H}/T^2] \, dT$$

If further, $\Delta_{vap}\boldsymbol{H}$ is nearly independent of temperature,

$$\boxed{\ln x_A = \Delta_{fus} \boldsymbol{H}/R \left[\frac{-1}{T} + \frac{1}{T^*} \right]}$$

Since $\ln x_A$ is negative, $T < T^*$.

The freezing point of the solution containing a non-volatile solute is lower than that of the pure solvent.

Sometimes, it makes sense to use some other unit of concentration than x_A. If we use *molality* instead, moles of solvent is [1000 g /Molecular Weight] and moles of solute is *m*:

$$x_A = \frac{1000/\mathrm{M}}{1000/\mathrm{M} + m} = [1+(m\mathrm{M}/1000)]^{-1}$$

$\ln x_A = -\ln[1+(\text{mM}/1000)]$

$$d\ln x_A = -\frac{\text{M}/1000}{[1+(m\text{M}/1000)]}\,dm$$

Put it into:

$d\ln x_A = (1/R)\,[\Delta_{fus}\boldsymbol{H}/T^2]\,dT$

and assume $\Delta_{fus}\boldsymbol{H}$ is independent of temperature,

$$-dT/dm = \frac{[\text{M}/1000]\,RT^2}{[1+(m\text{M}/1000)]\times\Delta_{fus}\boldsymbol{H}}$$

For very low solute concentrations, neglecting second term compared to 1:

$$-dT/dm = \frac{MRT^2}{1000\,\Delta_{fus}\boldsymbol{H}}$$

Let $K_f = \dfrac{MRT^{*2}}{1000\,\Delta_{fus}\boldsymbol{H}}$ for molality

For very small changes, then

$-\Delta T/m \approx K_f$

where $\Delta T = (T\text{-}T^*)$ *is the "freezing point depression"*

To summarize, *if the ΔT is sufficiently small*,

$$(T_f^* - T_f) = m_B K_f \quad \text{where } K_f = \frac{MRT^{*2}}{1000\,\Delta_{fus}\boldsymbol{H}}$$

$$(T_b - T_b^*) = m_B K_b \quad \text{where } K_b = \frac{MRT^{*2}}{1000\,\Delta_{vap}\boldsymbol{H}}$$

Otherwise,

$$\frac{mM}{1000} = \Delta_{fus}\boldsymbol{H}/R \left[\frac{1}{T_f} - \frac{1}{T_f^*} \right]$$

$$\frac{mM}{1000} = \Delta_{vap}\boldsymbol{H}/R \left[-\frac{1}{T_b} + \frac{1}{T_b^*} \right]$$

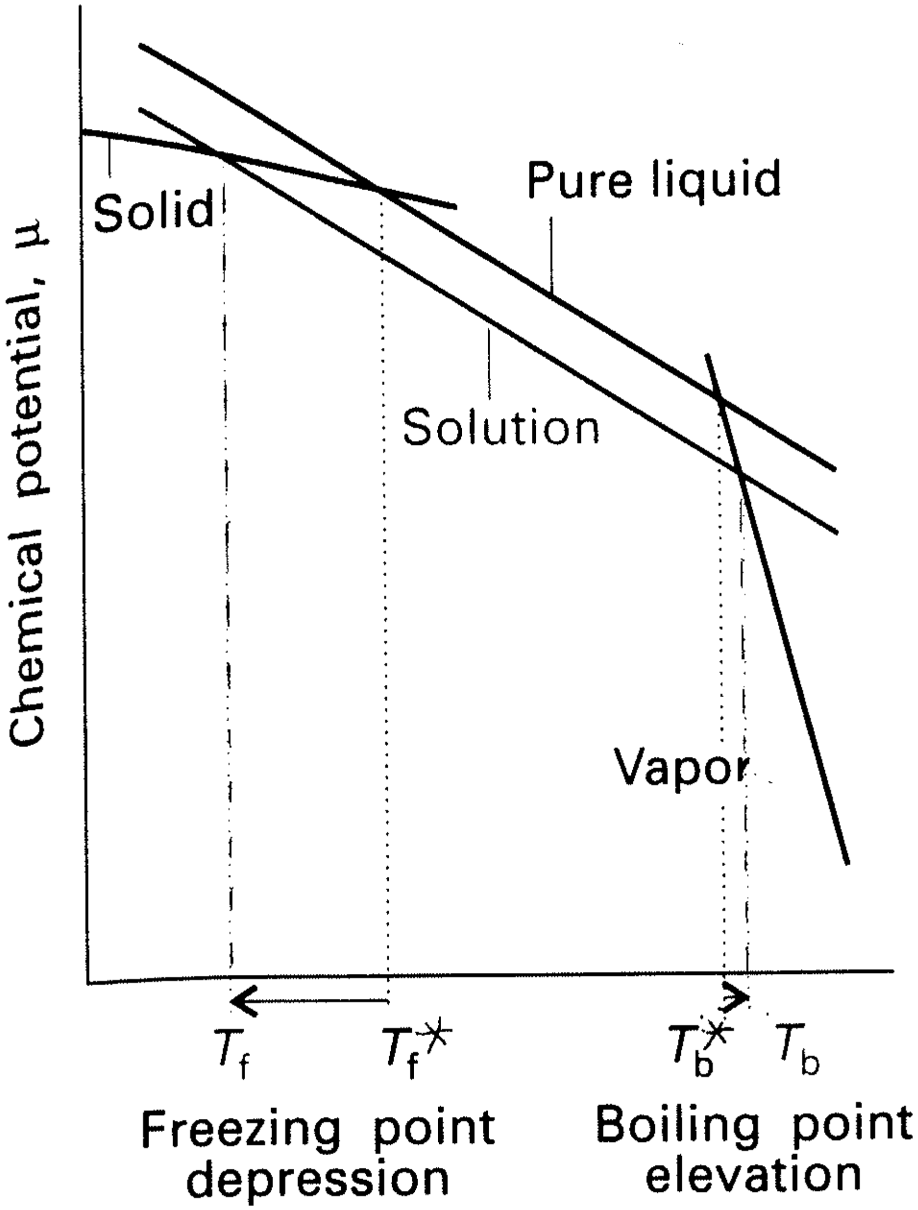
When the solute is non-volatile (does not have a contribution to the vapor pressure), then the vapor pressure of the solution is lower than that of the pure solvent:

If ideal solution behavior is observed, the vapor pressure over the solution, p is less than that of the pure solvent p^*_A

$$p/p^*_A = x_A .$$

To reach the same total vapor pressure (1 atm) it will be necessary to take the solution to a higher temperature, so the boiling point of the solution is higher than the pure solvent.

The chemical potential of a solvent in the presence of a solute. The lowering of the chemical potential of the liquid has a greater effect on the freezing point than on the boiling point because the angles at which the lines intersect are determined by ***S***.



Osmotic pressure

When a semipermeable membrane separates a solution from the pure solvent, the membrane being permeable only to the solvent, the solvent will flow from the pure solvent side to the solution side until μ_A is the same on both sides.

The *additional pressure* that needs to be applied *to the solution side* to achieve equilibrium is the "***osmotic pressure***".

In equilibrium with this solution is pure solvent at pressure *p*,

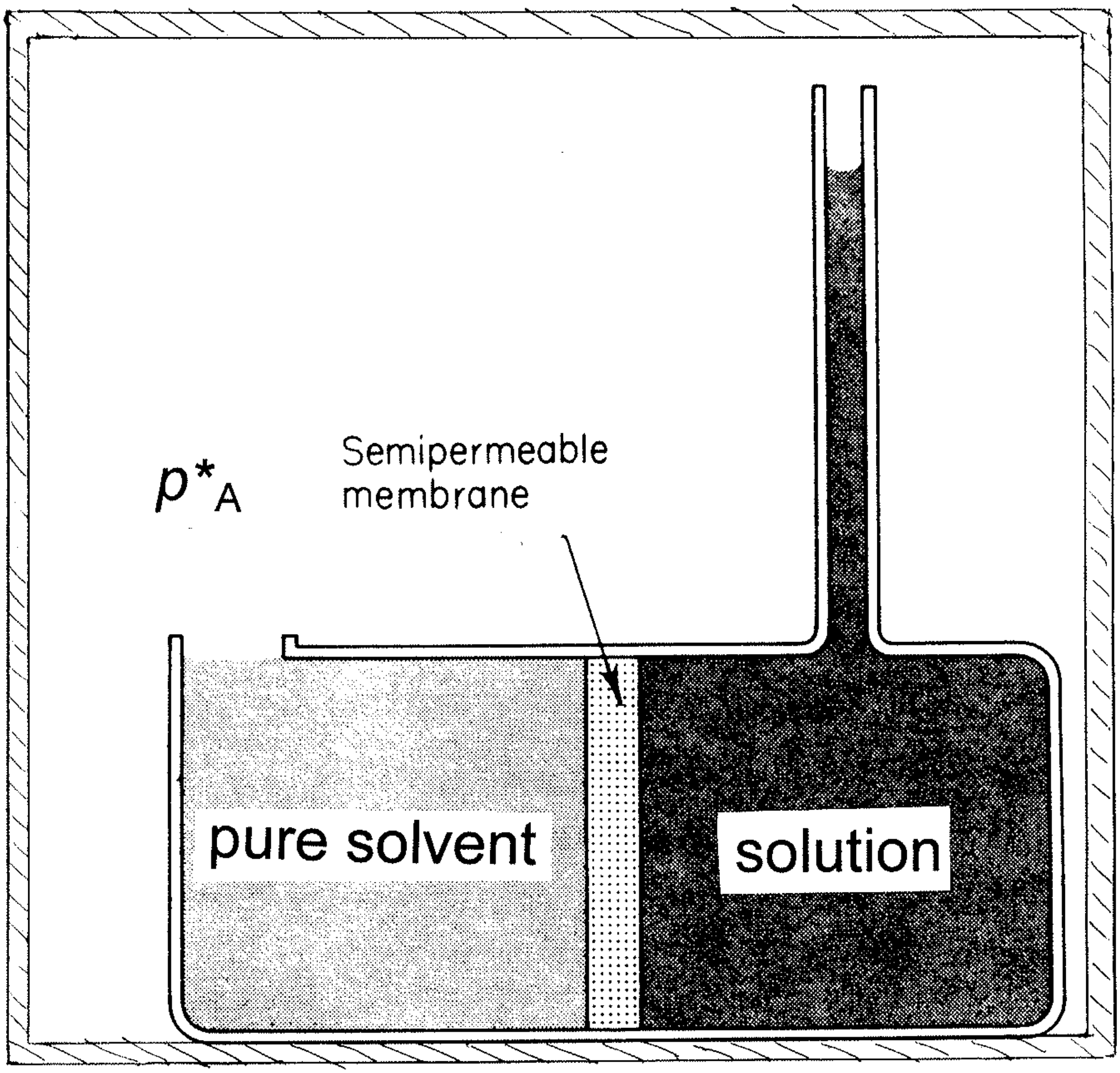
❀ $\mu_{\text{A, liquid}}(T,p+\pi,x_A) = \mu^*_{\text{A, liquid}}(T,p)$ (1)

If the solution is ideal, then

$\mu_{\text{A,liquid}} = \mu^*_{\text{A,liquid}} + RT\ln x_A$ (ideal solution)

specifically,

$$\mu_{\text{A,liquid}}(T,p+\pi,x_A) = \mu^*_{\text{A,liquid}}(T,p+\pi) + RT\ln x_A \quad (2)$$


p^*_A
Semipermeable membrane
pure solvent
solution

Eq. (2) substituted into (1) gives:

$\mu^*_{\mathrm{A,liquid}}(T,p+\pi) + RT \ln x_A = \mu^*_{\mathrm{A,liquid}}(T,p)$

rearrange to:

$\mu^*_{\mathrm{A,liquid}}(T,p+\pi) - \mu^*_{\mathrm{A,liquid}}(T,p) = -RT \ln x_A$

Look at LHS, pure liquid solvent

Since $(\partial\mu/\partial p)_T = V_m$,

the left hand side is

$$\int_p^{p+\pi} V_m \, \mathrm{d}p = V_m (p+\pi - p) = V_m \pi$$

$\therefore V_m \pi = -RT \ln x_A$

$\ln x_A = \ln(1-x_B)$

$\approx -x_B - (1/2)x_B^2 - (1/3)x_B^3 - (1/4)x_B^4 - \ldots$

$$\boxed{V_m \pi = RTx_B}$$

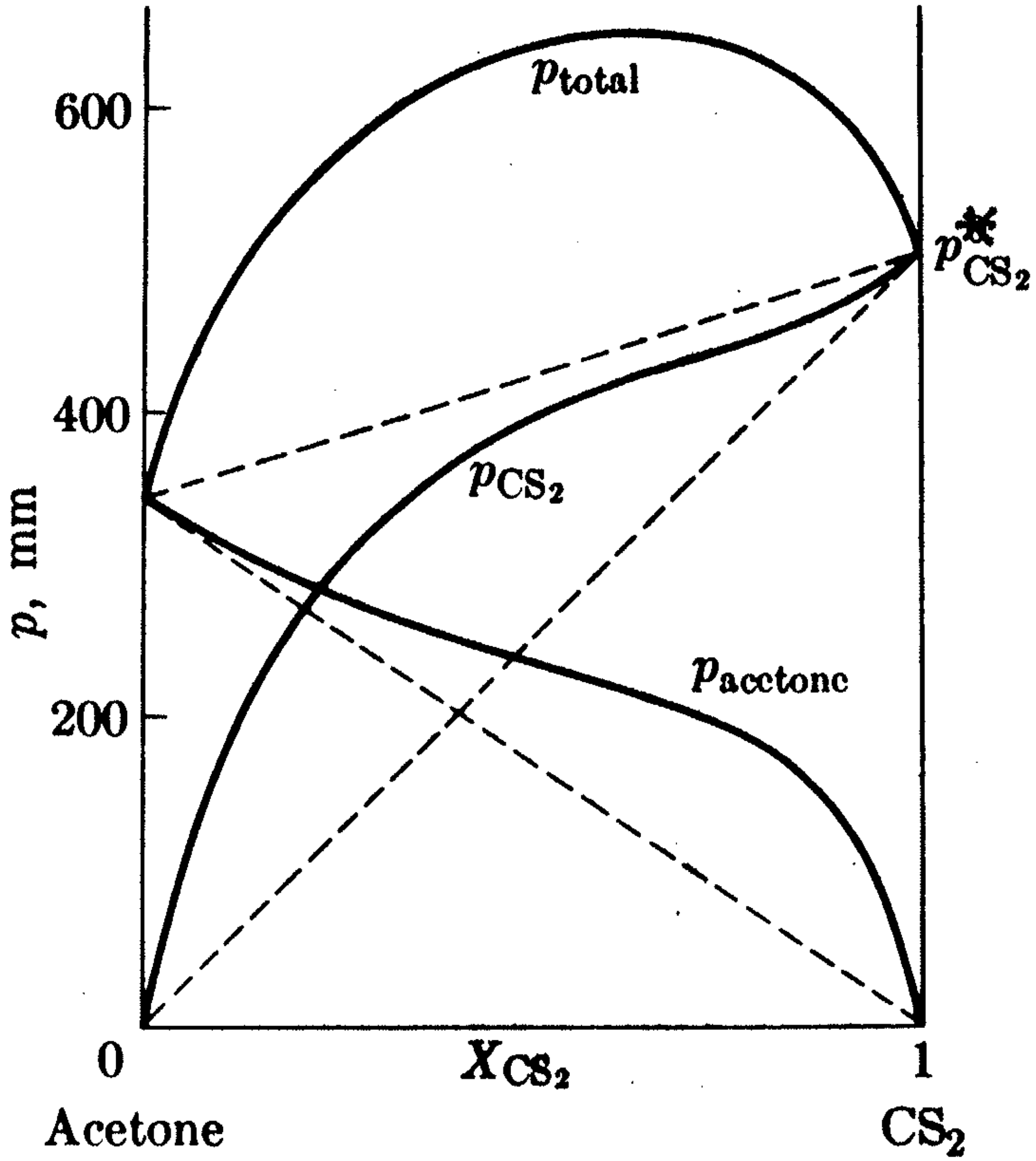
Substitute $x_B = n_B/(n_A+n_B) \approx n_B/n_A$ to get

$$\pi n_A V_m = n_B RT$$

or $\pi = C_B RT$	***osmotic pressure***
	<u>molarity</u> is C_B
or $V_m \pi = (RTM/1000)\, m_B$	molality is m_B

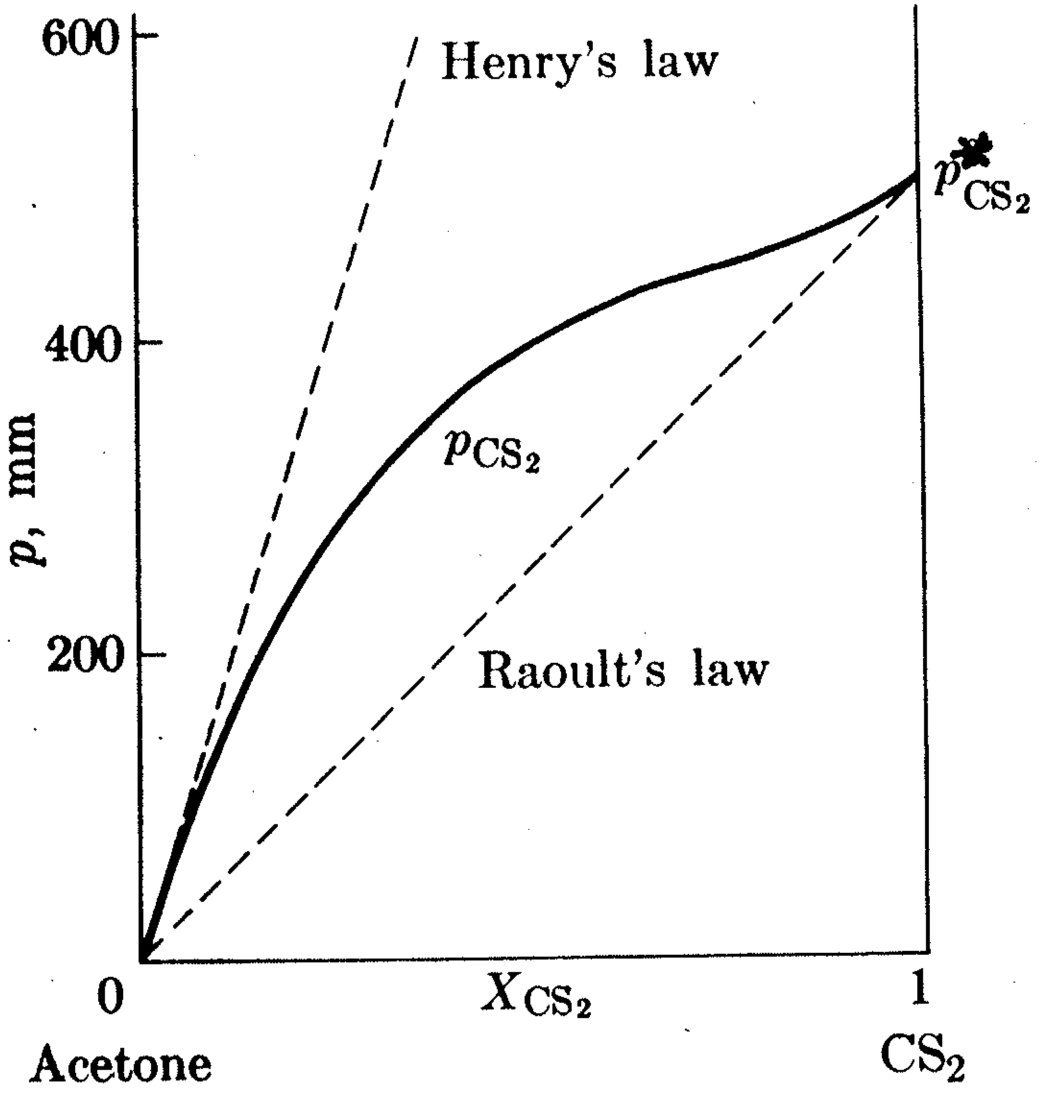
7.6 Equilibria in Non-Ideal Systems: The Concept of Activity a_i, (the Rational System, or the Practical System, or in terms of Molalities)

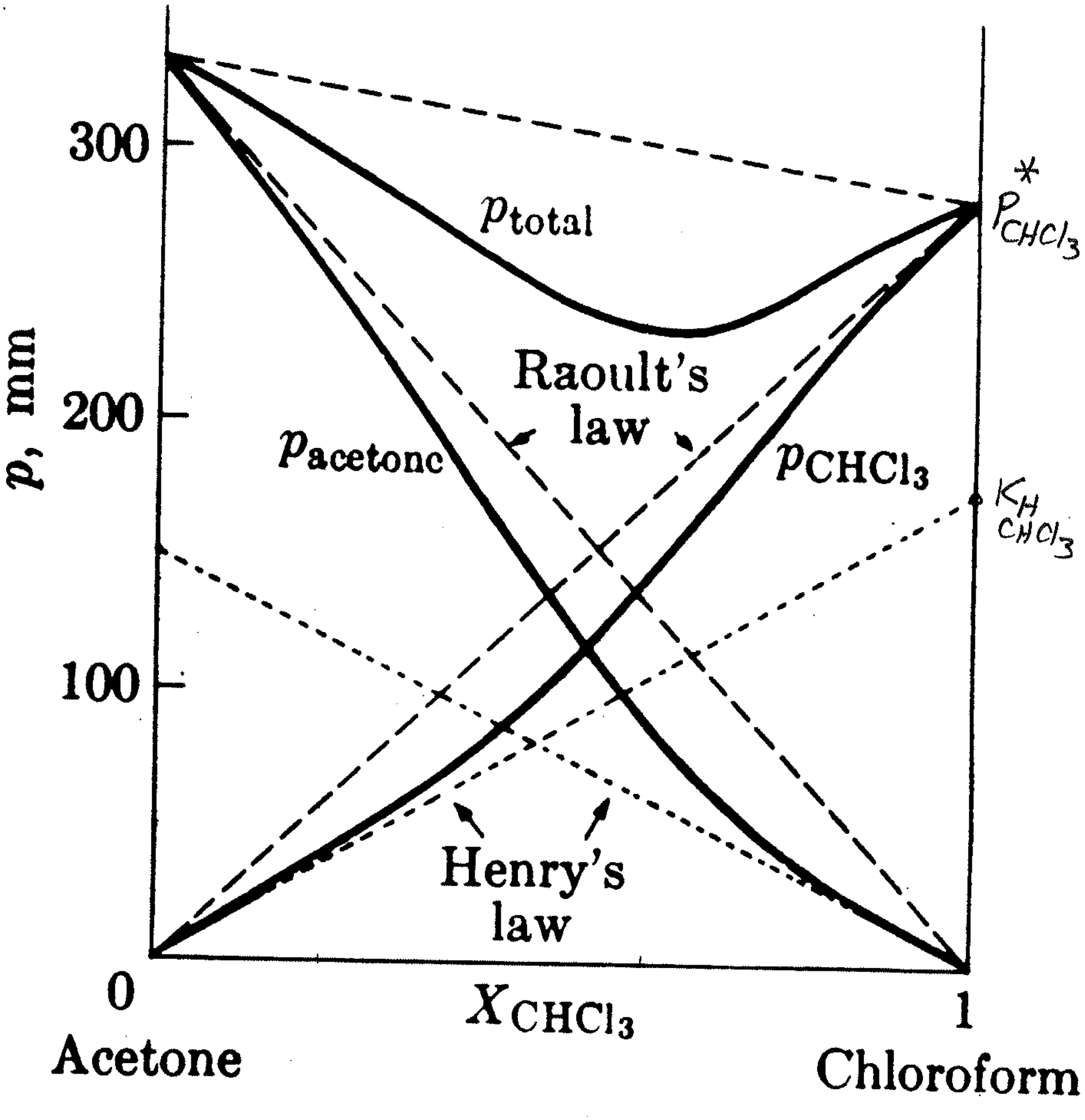
Non-ideal solutions



Near $x_A = 1$, $p_A = p^*_A x_A$ Raoult's law

Near $x_A = 0$, $p_A = K_{H,A} x_A$ Henry's Law




300
200
100
p, mm
p_{total}
$p_{acetone}$
p_{CHCl_3}
Raoult's law
Henry's law
$P^*_{CHCl_3}$
K_H $CHCl_3$
0
X_{CHCl_3}
1
Acetone
Chloroform

xtra

The concept of activity

For the gas, we have already defined activity:

$$\mu(T) = \mu^{\ominus}_{T} + RT \ln \frac{f}{1} \qquad \text{(real gas)}$$

For more than one component in a gas mixture,

$$\mu_i(T,p,x) = \mu_i{}^{\ominus}{}_{T} + RT \ln \frac{f_i}{1} (T,p,x)$$

Define activity for a liquid solution,

$$\mu_i(T,p,x) = g_i(T,p) + RT \ln \boldsymbol{a}_i (T,p,x)$$

This definition of activity states the *equivalence of the activity to the chemical potential*. All the dependence on the composition is contained in the activity. Various activity definitions correspond to the identification of $g_i(T,p)$.

Three systems of defining activity:

- rational system
- practical system
- molality-based

In each case, we define the "ideal system" used to define the limiting case and then compare this with the real system to define the activity. Along the way $g_i(T,p)$.is defined too.

<u>Rational system</u>:

Start with

$\mu_A(T,p,x) - \mu_A{}^*(T,p) = RT\ln(p_A/p^*_A)$

Raoult's law gives $(p_A/p^*_A) = x_A$

The rational system is based a solution that obeys Raoult's law (for all x) as a limiting case.

$\mu_{A,\ ideal}(T,p,x) = \mu_A{}^*(T,p) + RT\ln x_A$

For the real solution,

$\mu_A(T,p,x) = g_A(T,p) + RT\ln \boldsymbol{a}_A(T,p,x)$

Identify $g_A(T,p)$ as the chemical potential of the pure liquid, $\mu_A{}^*(T,p)$ so that for ideal solutions, $\boldsymbol{a}_A$ approaches x_A.

$$\boxed{\mu_A\,(T,p,x) = \mu_A{}^*(T,p) + RT\ln \boldsymbol{a}_A \quad \textit{(non-ideal solution)}}$$

Since $\mu_A\,(T,p,x) \rightarrow \mu_A{}^*(T,p)$ as $x_A \rightarrow 1$, this means $\boldsymbol{a}_A = 1$ for the pure liquid.

$$\mu_A\,(T,p,x) - \mu_{A\,(ideal)}(T,p,x) = RT\ln(\boldsymbol{a}_A/x_A)$$

Define the ratio $(\boldsymbol{a}_A/x_A) = \gamma_A$, the rational activity coefficient of component A, that which when multiplied by x_A turns it into activity.

$\gamma_A = (\boldsymbol{a}_A/x_A)$ $\gamma_A \rightarrow 1$ as $x_A \rightarrow 1$ rational

The solution in equilibrium with vapor,

$$\mu_A(T,p,x) = \mu_A{}^*(T,p) + RT\ln \boldsymbol{a}_A$$

$$= \mu_{A,\,gas}{}^*(T,p) + RT\ln(\boldsymbol{f}_A/1)$$

and for the pure liquid in equil. w/ vapor,

$$\mu_A{}^*(T,p) = \mu_{A,\,gas}{}^*(T,p) + RT\ln(\boldsymbol{f}_A{}^*/1)$$

Putting these together, we find

$\ln \boldsymbol{a}_A = \ln(\boldsymbol{f}_A/\boldsymbol{f}_A{}^*)$,

$$\therefore \boldsymbol{a}_A = (\boldsymbol{f}_A/\boldsymbol{f}_A{}^*)$$

or $\boldsymbol{a}_A = p_A/p_A{}^*$ *if the vapor is an ideal gas.*

To find $\boldsymbol{a}_A$ we need to measure partial vapor pressures or colligative properties for the solution:

$$\ln \boldsymbol{a}_A = \Delta_{fus}\boldsymbol{H}/R\left[-\frac{1}{T_f} + \frac{1}{T_f{}^*}\right]$$

$$\ln \boldsymbol{a}_A = \Delta_{vap}\boldsymbol{H}/R\left[\frac{1}{T_b} - \frac{1}{T_b{}^*}\right]$$

$$V_m\,\pi = -RT\ln \boldsymbol{a}_A$$

Now to find out how to get $\boldsymbol{a}_B$

The solution in equilibrium with vapor,

$$\mu_B(T,p,x) = \mu_B{}^*(T,p) + RT\ln K_H/p_B{}^* + RT\ln \boldsymbol{a}_B$$
$$= \mu_{B,\,gas}{}^*(T,p) + RT\ln(\boldsymbol{f}_B/1)$$

and for the pure liquid in equil. w/ vapor,

$$\mu_B{}^*(T,p) = \mu_{B,\,gas}{}^*(T,p) + RT\ln(\boldsymbol{f}_B{}^*/1)$$

Putting these together,

$$\ln \boldsymbol{a}_B = \ln(\boldsymbol{f}_B p_B{}^*/\boldsymbol{f}_B{}^* K_H)$$

$$\boxed{\therefore \boldsymbol{a}_A = (\boldsymbol{f}_B\, p_B{}^*/\boldsymbol{f}_B{}^* K_H)}$$

or $\boldsymbol{a}_B = p_B/K_H$ *if the vapor is an ideal gas.*

Can also obtain $\boldsymbol{a}_B$ from colligative properties, simply replace in previously derived expressions

$$\ln x_A = \ln(1-x_B)$$
$$\approx -x_B - (1/2)x_B^2 - (1/3)x_B^3 - (1/4)x_B^4 - \ldots$$

and then replace x_B by $\boldsymbol{a}_B$. For example,

$$\boxed{V_m \pi = RT\, \boldsymbol{a}_B \quad \text{osmotic pressure}}$$

Practical system:

For the solute:

For solutions in which only the solvent has a molefraction close to 1, we need a practical system for the solutes.

$\mu_B(T,p,x) = g_B(T,p) + RT \ln \boldsymbol{a}_B (T,p,x)$

$\mu_B (T,p,x) - \mu_{B\ (ideal)}(T,p,x) = RT \ln (\boldsymbol{a}_B / x_B)$

where $\gamma_B = (\boldsymbol{a}_B / x_B)$. However, as $x_B \to 0$ this becomes indeterminate, we need to find the correct limiting behavior.

Let $g_B(T,p)$ be the chemical potential of a hypothetical ideal solution that obeys Henry's law all the way. Using Henry's law $p_B = K_H\, x_B$ for the ideal case:

$$\mu_{B,\ ideal}(T,p,x) = \mu_B^*(T,p) + RT \ln K_H/p_B^* + RT \ln x_B$$

Compare with,

$\mu_B(T,p,x) = g_B(T,p) + RT \ln \boldsymbol{a}_B (T,p,x)$

Thus, the choice for the solute is

$g_B(T,p) = \mu_B^*(T,p) + RT \ln K_H/p_B^*$

For the real solution,

$$\mu_B(T,p,x) = \mu_B{}^*(T,p) + RT \ln K_H/p_B{}^* + RT \ln \boldsymbol{a}_A\,(T,p,x)$$

$$\mu_B\,(T,p,x) - \mu_{B\ (ideal)}(T,p,x) = RT \ln(\boldsymbol{a}_B\,/x_B)$$

As the ideal case is approached, i.e., as B in the real solution behaves like Henry's law,

$\boldsymbol{a}_B \rightarrow x_B$ as $x_B \rightarrow 0$

Define the ratio $(\boldsymbol{a}_B\,/x_B) = \gamma_B$, the activity coefficient of component B, that which when multiplied by x_B turns it into activity.

$$\gamma_B = (\boldsymbol{a}_B\,/x_B) \quad \gamma_B \rightarrow 1 \text{ as } x_B \rightarrow 0$$

$$\boxed{\begin{aligned} \boldsymbol{a}_B &= \Delta_{fus}\boldsymbol{H}/R\left[\frac{1}{T_f} - \frac{1}{T_f^*}\right] \\ \boldsymbol{a}_B &= \Delta_{vap}\boldsymbol{H}/R\left[-\frac{1}{T_b} + \frac{1}{T_b^*}\right] \end{aligned}}$$

Practical system based on molality:

For solutions in which only the solvent has a molefraction close to 1, we need a practical system for the solutes. As in above,

$$\mu_B(T,p,x) = g_B(T,p) + RT \ln \boldsymbol{a}_B(T,p,x)$$

Let $g_B(T,p)$ be the chemical potential of a hypothetical ideal solution of unit molality that obeys Henry's law, Using Henry's law for p_B, but expressed in molality rather than molefraction,

$p_B = K'_H m_B$ for the ideal case:

$$\mu_{B,\,ideal}(T,p,x) = \mu_B^*(T,p) + RT \ln K'_H/p_B^* + RT \ln m_B$$

Compare with,

$\mu_B(T,p,x) = g_B(T,p) + RT \ln \boldsymbol{a}_B (T,p,x)$

Thus, the choice for the solute is

$g_B(T,p) = \mu_B{}^*(T,p) + RT \ln K'_H/p_B{}^*$

For the real solution,

$$\mu_B(T,p,x) = \mu_B{}^*(T,p) + RT \ln K'_H/p_B{}^* + RT \ln \boldsymbol{a}_A (T,p,x)$$

$\mu_B (T,p,x) - \mu_{B\ (ideal)}(T,p,x) = RT \ln(\boldsymbol{a}_B / m_B)$

As the ideal case is approached, i.e., as B in the real solution behaves like Henry's law,

$\boldsymbol{a}_B \rightarrow m_B$ as $m_B \rightarrow 0$

Define the ratio $(\boldsymbol{a}_B / m_B) = \gamma_B$, the activity coefficient of component B, that which when multiplied by m_B turns it into activity.

$$\gamma_B = (\boldsymbol{a}_B / m_B)\ \gamma_B \rightarrow 1 \text{ as } m_B \rightarrow 0$$

Now to find out how to get $\boldsymbol{a}_B$

The solution in equilibrium with vapor,

$$\mu_B(T,p,x) = \mu_B{}^*(T,p) + RT \ln K'_H/p_B{}^* + RT \ln \boldsymbol{a}_B$$

$$= \mu_{B,\ gas}{}^*(T,p) + RT \ln(\boldsymbol{f}_B/1)$$

and for the pure liquid in equil. w/ vapor,

$$\mu_B{}^*(T,p) = \mu_{B,\ gas}{}^*(T,p) + RT \ln(\boldsymbol{f}_B{}^*/1)$$

Putting these together,

$$\ln \boldsymbol{a}_B = \ln(\boldsymbol{f}_B p_B{}^*/\boldsymbol{f}_B{}^* K'_H)$$

$\therefore \boldsymbol{a}_B = (\boldsymbol{f}_B\, p_B{}^*/\boldsymbol{f}_B{}^* K'_H)$

or $\boldsymbol{a}_B = p_B/K'_H$ *if the vapor is an ideal gas.*

Can also obtain $\boldsymbol{a}_B$ from colligative properties, simply replace m_B by $\boldsymbol{a}_B$ in previously derived expressions

$V_m\,\pi = (RTM/1000)\,\boldsymbol{a}_B$ osmotic pressure

$$\boldsymbol{a}_B = \frac{1000\Delta_{fus}\boldsymbol{H}/R}{M}\left[\frac{1}{T_f} - \frac{1}{T_f^*}\right]$$

$$\boldsymbol{a}_B = \frac{1000\Delta_{vap}\boldsymbol{H}/R}{M}\left[-\frac{1}{T_b} + \frac{1}{T_b^*}\right]$$

if ΔT is sufficiently small,

$(T^*-T) = \boldsymbol{a}_B K_f$ where $K_f = \dfrac{MRT^{*2}}{1000\,\Delta_{fus}\boldsymbol{H}}$

$(T-T^*) = \boldsymbol{a}_B K_b$ where $K_b = \dfrac{MRT^{*2}}{1000\,\Delta_{vap}\boldsymbol{H}}$

Summary of activities:

Definition	Rational	Practical
applied to	solvent	solute
basis	x_A	x_B
definition of activity a	$a_A \equiv f_A/f^*_A$ $[a_A = p_A/p^*_A]$	$a_B \equiv p_B/K_H$
definition of activity coeff γ	$\gamma_A \equiv a_A/x_A$	$\gamma_B \equiv a_B/x_B$
limiting behavior	as $x_A \to 1$ $\gamma_A \to 1$ $a_A \to x_A$	as $x_B \to 0$ $\gamma_B \to 1$ $a_B \to x_B$
how to measure a	$\ln a_A = -\Delta_{fus}H/R \cdot \{(1/T_f)-(1/T_f^*)\}$ $\ln a_A = -\Delta_{vap}H/R \cdot \{-(1/T_b)+(1/T_b^*)\}$ $\ln a_A = -V_m\pi/RT$ $a_A = p_A/p^*_A$	$a_B = \Delta_{fus}H/R \cdot \{(1/T_f)-(1/T_f^*)\}$ $a_B = \Delta_{vap}H/R \cdot \{-(1/T_b)+(1/T_b^*)\}$ $a_B = V_m\pi/RT$ $a_B \equiv p_B/K_H$

Summary of activities, solvent, solute

Definition	Rational	Practical
applied to→	solvent	solute
basis	x_A	x_B
basis	*Raoult*	*Henry*
definition of activity $\boldsymbol{a}$	$\boldsymbol{a}_A \equiv f_A/f^*_A$ $[\boldsymbol{a}_A = p_A/p^*_A]$	$\boldsymbol{a}_B \equiv p_B/K_H$
definition of activity coeff γ	$\gamma_A \equiv \boldsymbol{a}_A/x_A$	$\gamma_B \equiv \boldsymbol{a}_B/x_B$
limiting behavior $\gamma\to1$	as $x_A\to1$ $\gamma_A\to1$ $\boldsymbol{a}_A\to x_A$	as $x_B\to0$ $\gamma_B\to1$ $\boldsymbol{a}_B\to x_B$
ideal solution $\gamma=1$	$\boldsymbol{a}_{A,ideal}=x_A$	$\boldsymbol{a}_{B,\ ideal}=x_B$
$\boldsymbol{a}=1$, $\mu_T=\mu^\ominus_T$ for standard state at 1 bar	pure liquid *A* $\mu_A{}^\ominus_T=\mu_A{}^*_T$	fictitious solution having $p_B=K_H$

Summary of activities, solute:

Definition	Practical, m_B	Practical
applied to→	solute	solute
basis	m_B	x_B
basis	Henry	Henry
definition of activity a	$a_B \equiv p_B/K'_H$ $p_B = K'_H m_B$ $a_B \equiv \gamma_B(m_B/1)$	$a_B \equiv p_B/K_H$
definition of activity coeff γ	$\gamma_B \equiv a_B/m_B$	$\gamma_B \equiv a_B/x_B$
limiting behavior $\gamma \to 1$	as $x_B \to 0$ $\gamma_B \to 1$ $a_B \to m_B$	as $x_B \to 0$ $\gamma_B \to 1$ $a_B \to x_B$
ideal solution $\gamma = 1$	$a_{B,\,ideal} = m_B$	$a_{B,\,ideal} = x_B$
a =1 for standard state $\mu^{\ominus}_T$ at 1 bar	fictitious Henry's law solution of unit molality	fictitious solution having $p_B = K_H$

Summary of activities $\mu_T = \mu^{\ominus}_T + RT\ln a$

Definition		
applied to→	gas mixture	pure gas
standard state at 1 bar $\mu^{\ominus}_T$	fictitious pure gas at 1 bar behaving ideally	fictitious gas at 1 bar behaving ideally
definition of activity, a (or f fugacity for gases)	$a_A \equiv f_A$	$RT\ln a = \int V dp$ $a = f$ $\ln(f/p) \equiv \int_0^p [Z-1] dp/p$
definition of activity coeff γ	$\gamma_A \equiv f_A/p_A$	$\gamma \equiv f/p$
limiting behavior $\gamma \to 1$	as $p \to 0$ $\gamma_A \to 1$ $f_A \to x_A p$	as $p \to 0$ $\gamma \to 1$ $f \to p$
ideal gas $\gamma = 1$	$f_{A,ideal} = p_A = x_A p$	$f_{ideal} = p$

$$\mu_T = \mu^{\ominus}_T + RT\ln a$$

What is the nature of the state for which the chemical potential is $\mu^{\ominus}_T$, called the ***standard state***, that is, *the state of unit activity?*

Standard state (state for which a =1 at a pressure of 1 bar)

component	standard state	basis
solvent A $a_A \equiv p_A/p_A^*$	pure liquid A $\mu_A{}^{\ominus}{}_T = \mu_A{}^*{}_T$	Raoult
solute B $a_B \equiv p_B/K_H$	fictitious Henry's Law solution having $p_B = K_H$	Henry
solute B	fictitious Henry's law solution of unit molality	Henry
gas	hypothetical state in which the gas is at a pressure of 1 bar and behaving perfectly	fugacity

EXAMPLE:

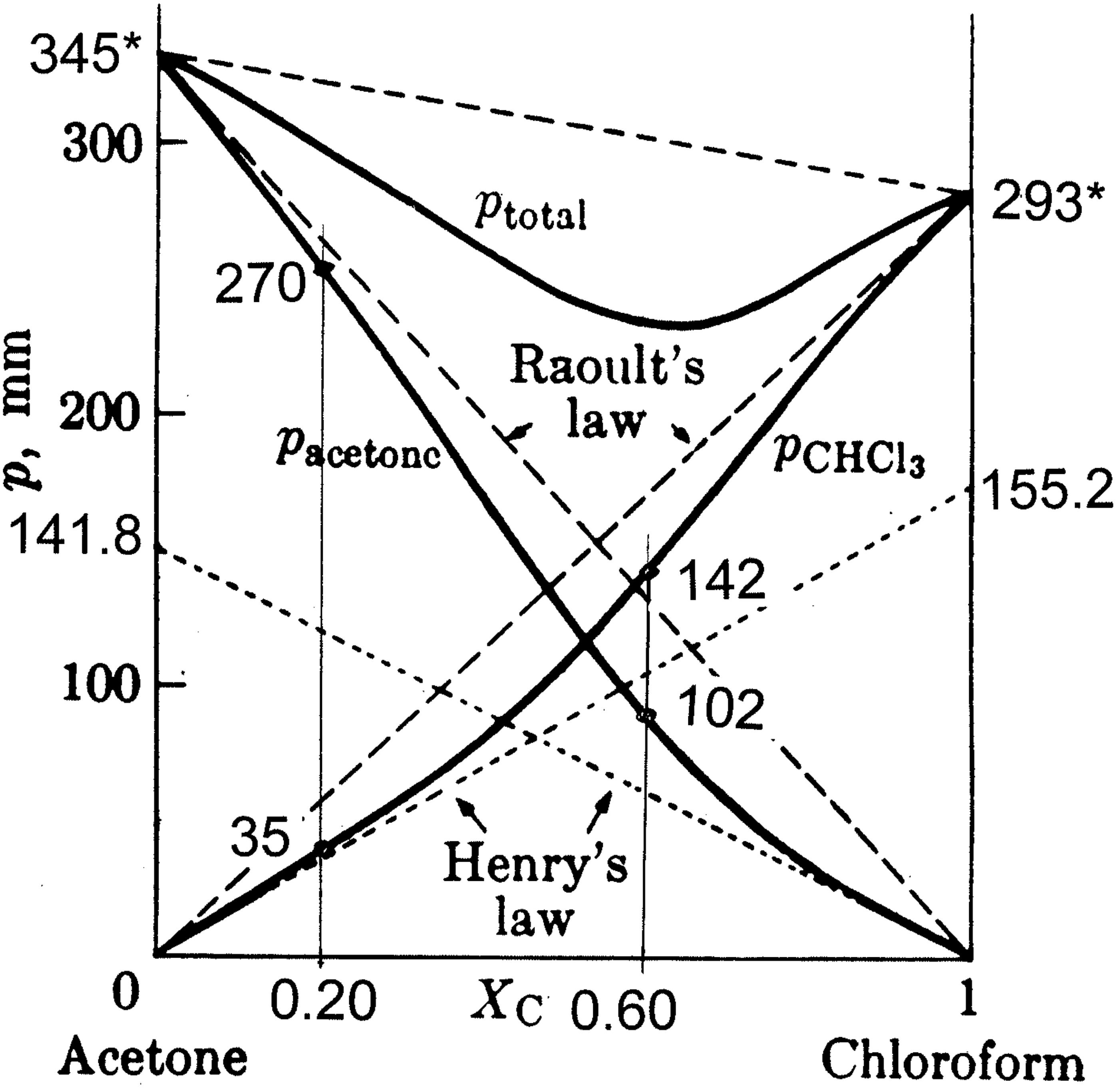
Calculate the ***activities*** a ***and activity coefficients*** γ ***in the rational system*** for the acetone-chloroform solution

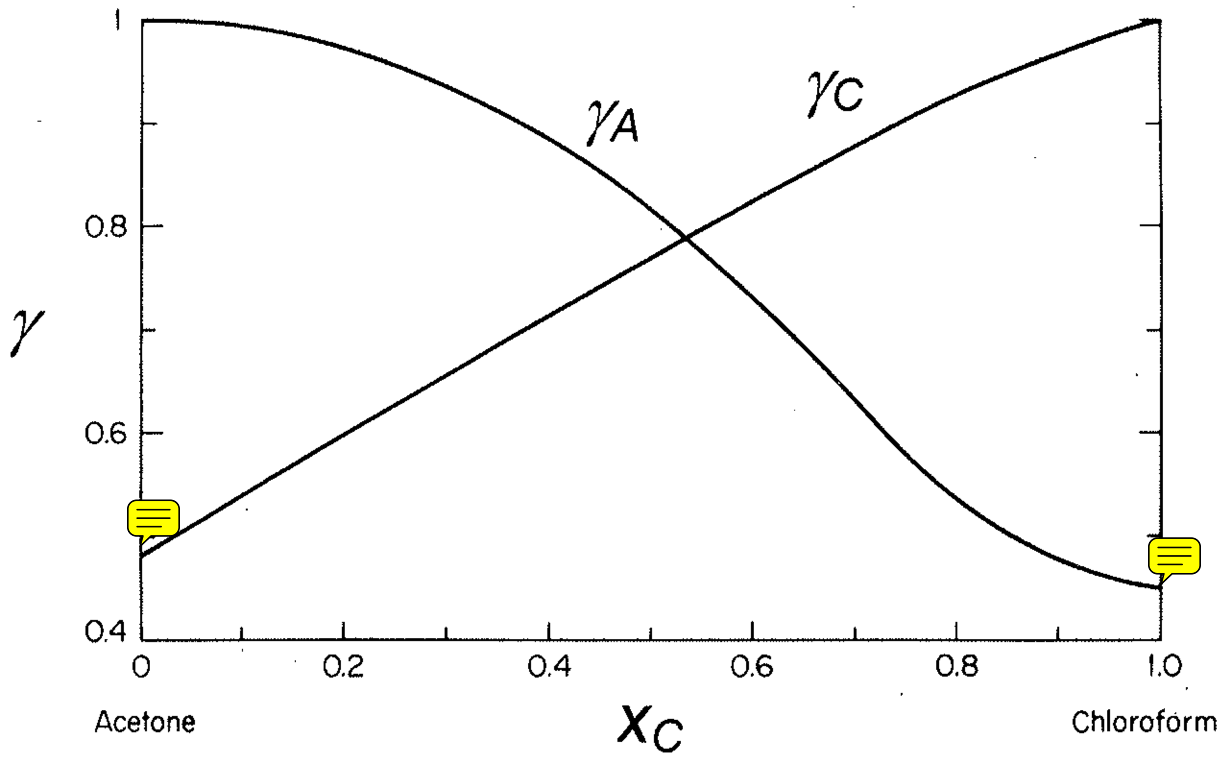
$K_{H,C}$	from p_C data at $x_C < 0.10$	141.8
$K_{H,A}$	from p_A data at $x_A < 0.10$	155.2

x_C	*given*	0.0	0.20	0.60	1.00
p_C	*given*	$x_C K_{HC}$	35	142	293*
p_A	*given*	345*	270	102	$x_A K_{HA}$

we get:

a_C	$= p_C / p^*_C$	0	0.120	0.485	1.00
a_A	$= p_A / p^*_A$	1.00	0.782	0.296	0
$p_{C,ideal}$	$x_C\, p^*_C$	0	59	176	293
$p_{A,ideal}$	$x_A\, p^*_A$	345	276	138	0
$\gamma_C = \dfrac{a_C}{a_{C,ideal}}$	$= a_C / x_C$ or $p_C / x_C\, p^*_C$	0.484	0.595	0.809	1.00 ideal in C
$\gamma_A = \dfrac{a_A}{a_{A,ideal}}$	$= a_A / x_A$ or $p_A / x_A\, p^*_A$	1.00 ideal in A	0.978	0.740	0.450


345*
300
p_{total}
293*
270
Raoult's law
200
p, mm
$p_{acetone}$
p_{CHCl_3}
155.2
141.8
142
100
102
35
Henry's law
0
0.20
X_C
0.60
1
Acetone
Chloroform


1
0.8
0.6
0.4
γ
γ_A
γ_C
0
0.2
0.4
0.6
0.8
1.0
Acetone
x_C
Chloroform