

STATISTICAL MOLECULAR THERMODYNAMICS

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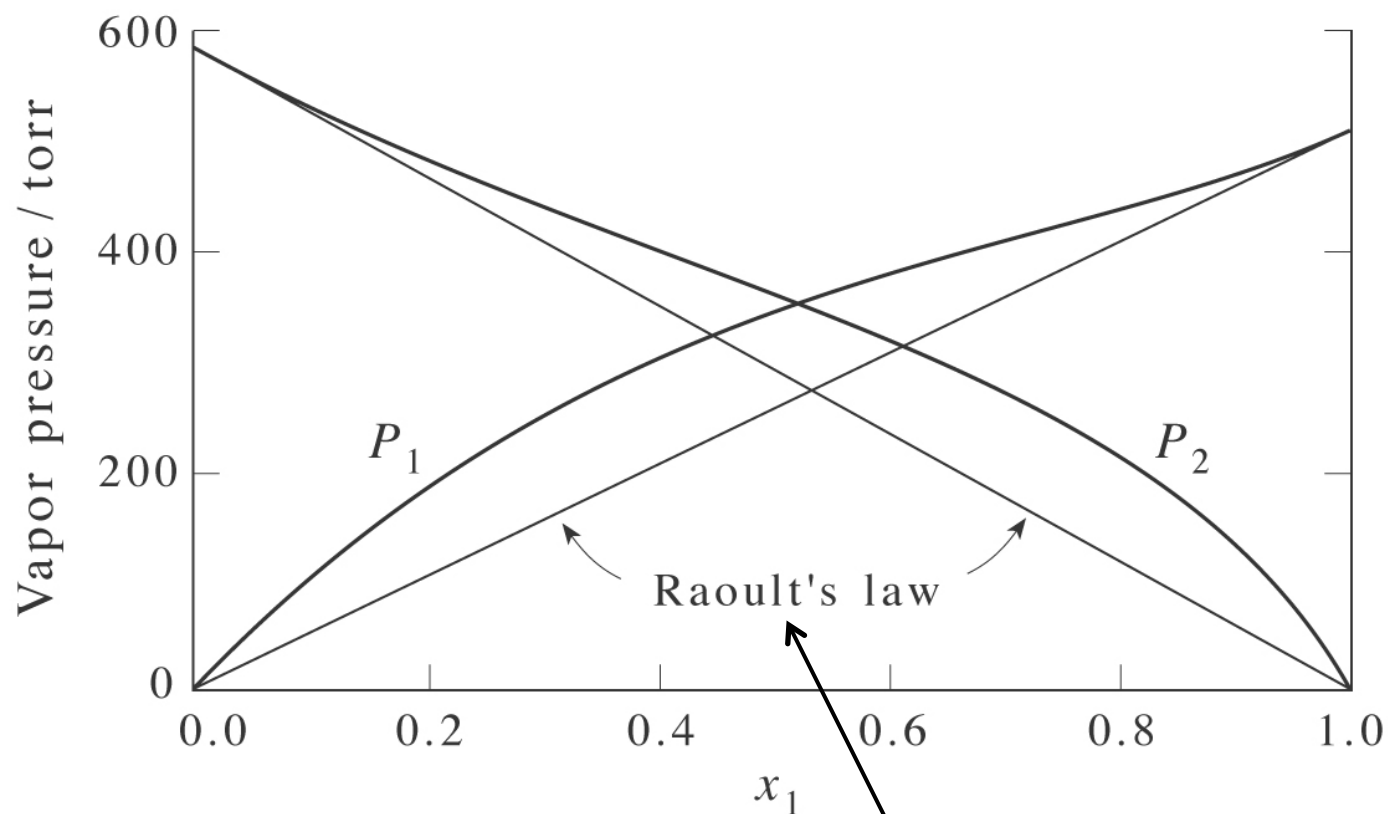
Video 10.6

Non-ideal Solutions

DEVIATIONS FROM RAOULT'S LAW

Carbon disulfide (CS_2) and dimethyl ether (CH_3OCH_3)

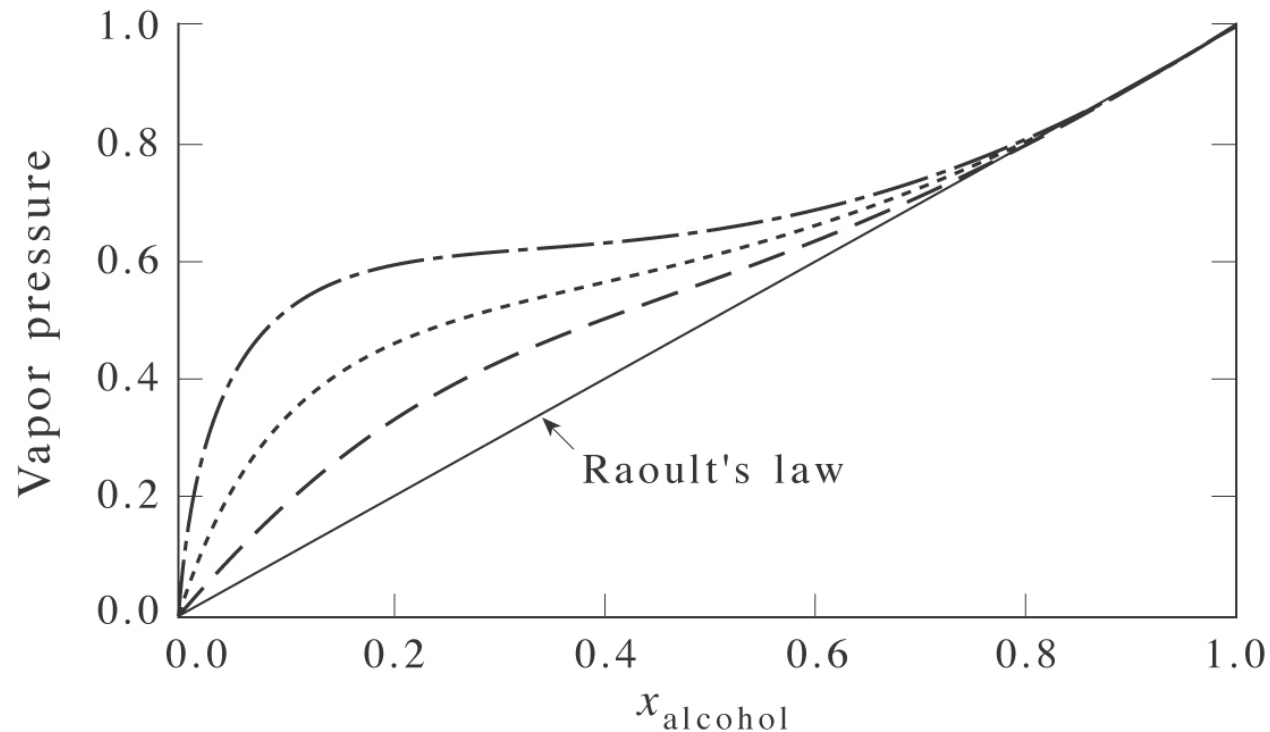
Actual behavior is “**positive deviation**” from Raoult’s Law. The molecules “don’t like each other” and leave solution *more* readily than predicted for an ideal solution



i.e., ideal behavior, $P_n = x_n P_n^*$

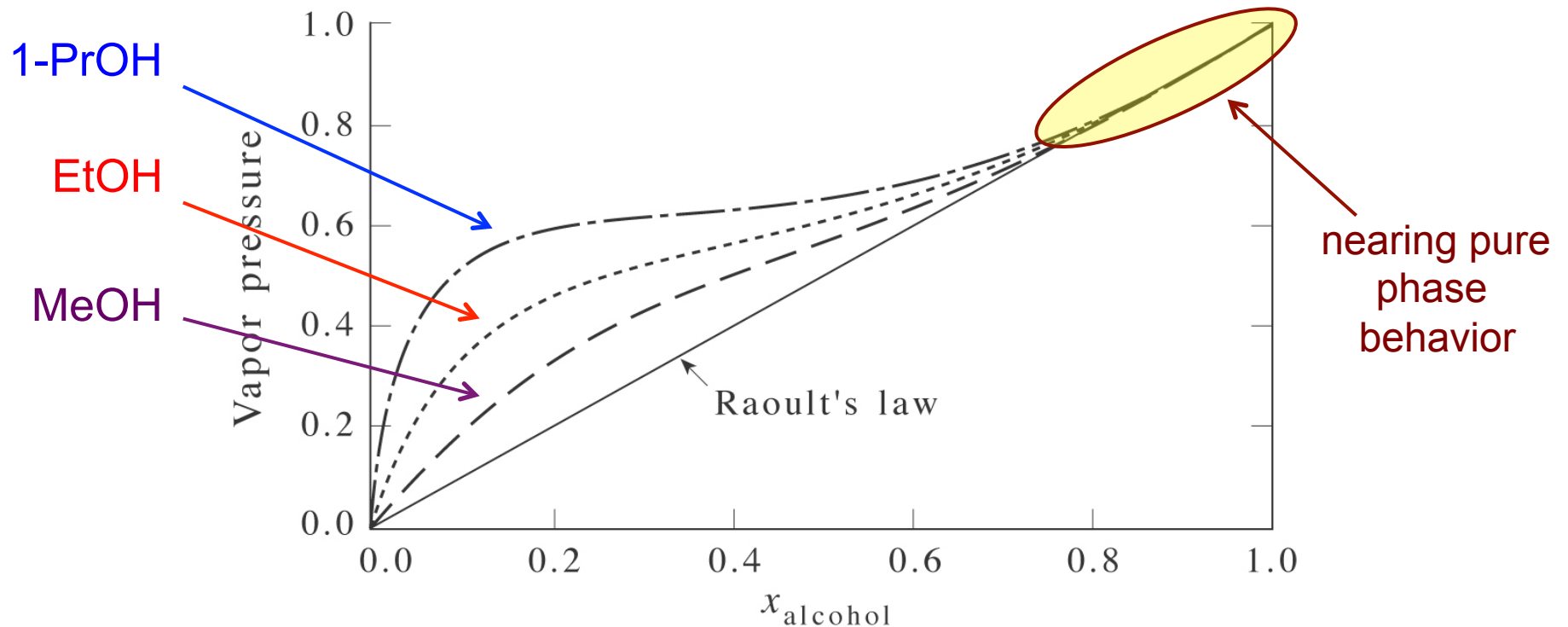
Self-assessment

Below are superimposed the liquid-vapor composition diagrams of MeOH:water, EtOH:water, and 1-PrOH:water. All show positive deviation from ideal behavior. Which do you assign as which and why? Also, rationalize the asymptotic behavior of the alcohol vapor pressure at high values of x_{alcohol} .



Self-assessment Explained

With increasing alkyl chain length, we would expect the hydrophobic effect to make the alcohol “like” water less, leading to increasingly positive deviations from ideal behavior. At the right asymptote, the solution is nearly alcohol in pure alcohol, so we expect an asymptotic approach to pure phase, ideal behavior, i.e., Raoult’s Law behavior.

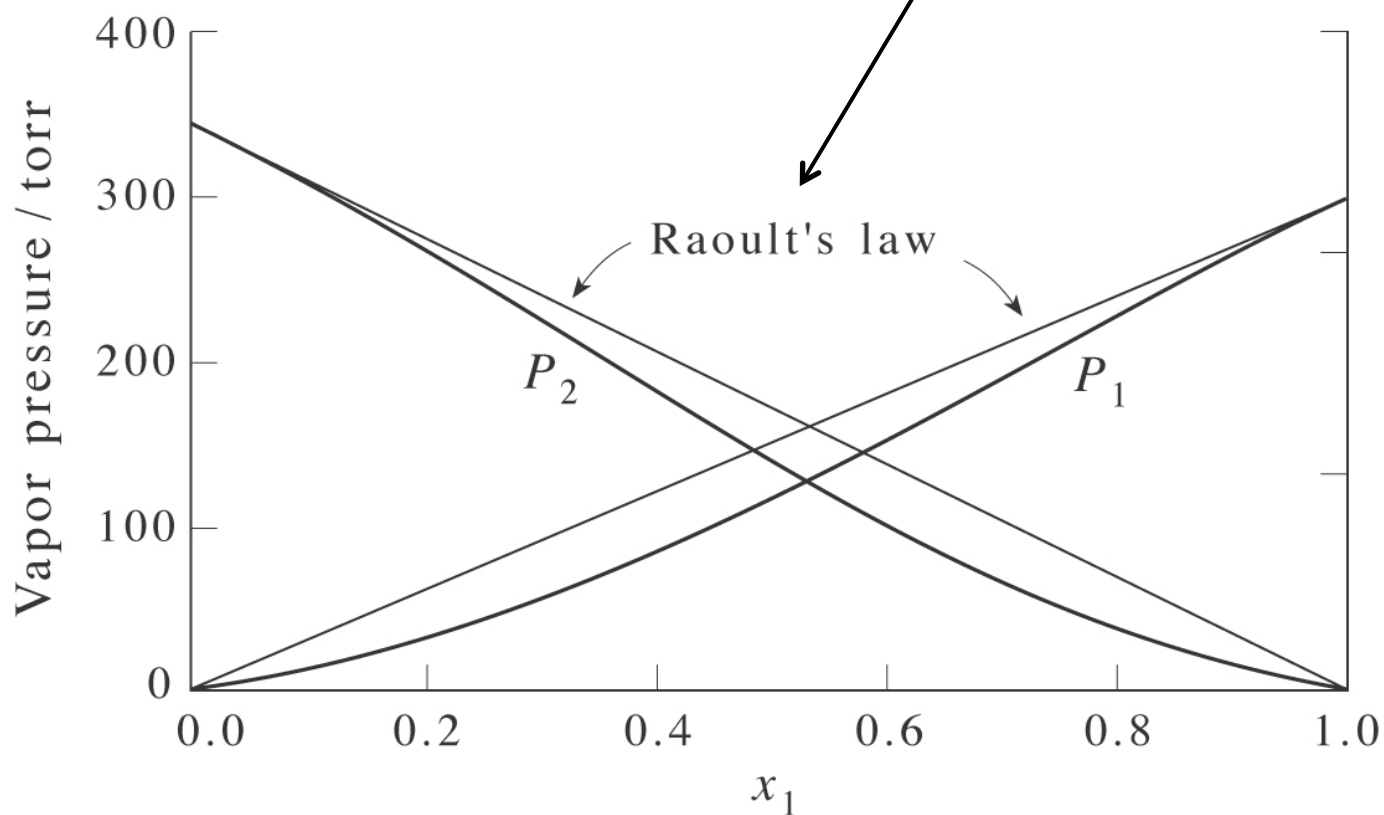


DEVIATIONS FROM RAOULT'S LAW 2

Chloroform (CHCl_3) and acetone ($(\text{CH}_3)_2\text{C}=\text{O}$)

i.e., ideal behavior, $P_n = x_n P_n^*$

Actual behavior is “**negative deviation**” from Raoult’s Law. The molecules “like each other a lot” and leave solution *less* readily than predicted for an ideal solution



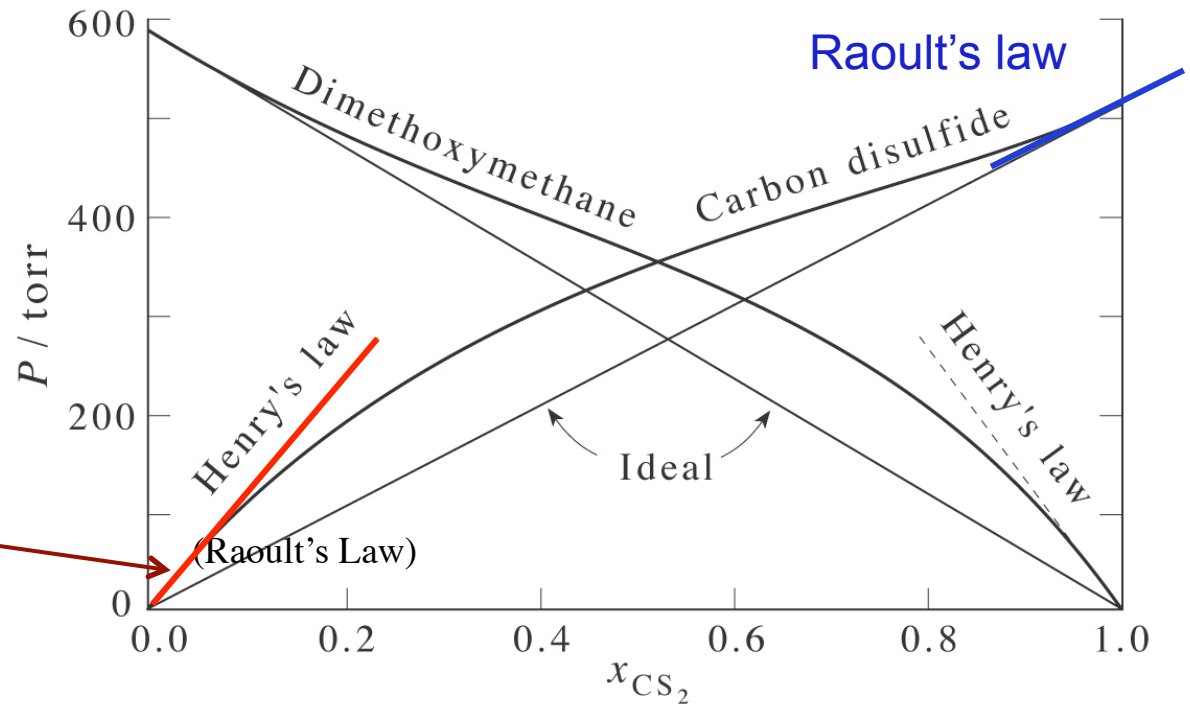
HENRY'S LAW

$$P_j \rightarrow x_j P_j^* \text{ as } x_j \rightarrow 1$$

Henry's law

$$P_j \rightarrow x_j k_{H,j} \text{ as } x_j \rightarrow 0$$

assessed from linear behavior of vapor pressure as function of mole fraction composition at near infinite dilution



Dilute slope is the “**Henry's law constant**”: $k_{H,j} \neq P_j^*$

Note that at low concentrations of component 1, all component 1 molecules are surrounded by component 2 molecules. The Henry's law constant is a measure of the *intermolecular* interactions between the two components.

RAOULT'S AND HENRY'S LAWS

Henry's Law behavior of 2 as $x_2 \rightarrow 0$ is a thermodynamic consequence of Raoult's Law behavior of 1 as $x_1 \rightarrow 1$.

Proof:

$$\mu_j(T, P) = \mu_j^\circ(T) + RT \ln P_j \quad \textit{ideal vapor}$$

so

$$d\mu_1 = RT \left(\frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} dx_1 \quad d\mu_2 = RT \left(\frac{\partial \ln P_2}{\partial x_2} \right)_{T,P} dx_2$$

recall Gibbs-Duhem equation

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

*establishes a relation
between the chemical
potentials of
components 1 and 2*

and substitute

RAOULT'S AND HENRY'S LAWS 2

after substitution and division of both sides by RT :

$$x_1 \left(\frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} dx_1 + x_2 \left(\frac{\partial \ln P_2}{\partial x_2} \right)_{T,P} dx_2 = 0$$

by definition of mole fraction $x_1 = 1 - x_2 \Rightarrow dx_1 = -dx_2$

so

$$x_1 \left(\frac{\partial \ln P_1}{\partial x_1} \right)_{T,P} = x_2 \left(\frac{\partial \ln P_2}{\partial x_2} \right)_{T,P}$$

When $P_1 \rightarrow 1$, becoming ideal, $P_1 \rightarrow x_1 P_1^*$ (Raoult's Law), thus

$$x_1 \left(\frac{\partial \ln P_1}{\partial x_1} \right)_{\lim x_1 \rightarrow 1} = x_1 \left(\frac{\partial \ln x_1 P_1^*}{\partial x_1} \right) = x_1 \left(\frac{1}{x_1} + 0 \right) = 1$$

RAOULT'S AND HENRY'S LAWS 3

Substitution again:

$$x_2 \left(\frac{\partial \ln P_2}{\partial x_2} \right)_{T,P} = 1 \quad \Rightarrow \quad \partial \ln P_2 = \frac{1}{x_2} \partial x_2$$

taking the indefinite integral of both sides

$$\ln P_2 = \ln x_2 + C$$

If we define $k_{H,2} = e^C$

$$\ln P_2 = \ln x_2 + \ln k_{H,2} = \ln(x_2 k_{H,2}) \quad \Rightarrow \quad P_2 = x_2 k_{H,2}$$

Completing the proof that as component 2 becomes infinitely dilute, Raoult's Law behavior for component 1 dictates Henry's Law behavior for component 2. **Q.E.D.**

Self-assessment

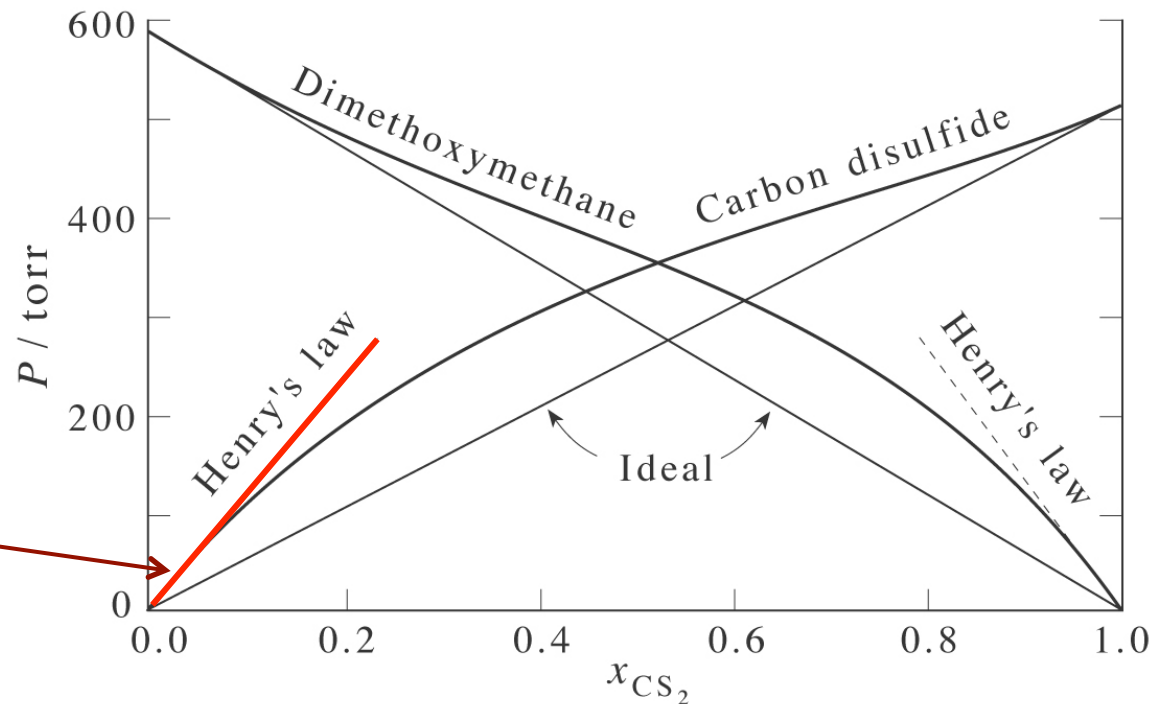
What units does $k_{H,2}$ have? Describe qualitatively its magnitude in terms of the pure component 2 vapor pressure in an ideal solution, a solution showing negative deviation from Raoult's Law, and a solution showing positive deviation from Raoult's Law.

Self-assessment Explained

Since mole fraction is a dimensionless number, Henry's Law implies $k_{H,2}$ must have units of pressure. To exhibit Raoult's Law behavior, the slope of the vapor pressure line must be P_2^* , so that is the value of $k_{H,2}$ for an ideal solution. Solutions showing positive and negative deviations from Raoult's law behavior would thus have $k_{H,2}$ values larger and smaller than P_2^* , respectively.

Henry's law
 $P_j \rightarrow x_j k_{H,j}$ as $x_j \rightarrow 0$

*assessed from linear behavior
of vapor pressure as function of
mole fraction composition at
near infinite dilution*



$$dU = \delta q + \delta w$$



Next: Azeotropes and Immiscible Phases