

SOLVENT TRANSFER ^{08 25-1} (Cont'd)

361 Lec24
Mon 16oct17

Case 1 Vapor Pressure of Pure Solvent



$$Q = \frac{\gamma_A P_A(g)}{1} \quad K_{eq} = (P_A)_{eq} = \text{''Vap. Press''}$$

Case 2: Vapor. Press. of Impure Solvent



$$Q = \frac{\gamma_{A(g)} P_{A(g)}}{\gamma_{A(l)} X_{A(l)}} \approx \frac{P_{A(g)}}{X_{A(l)}} \quad (\text{if ideal})$$

Equilibrium: $K = \left(\frac{P_{A(g)}}{X_{A(l)}} \right)_{eq}$ Vap. Press of the Solution

But $\Delta G^\circ = -RT \ln K$ always

or $K = e^{-\frac{\Delta G^\circ}{RT}}$ independent of X_A

i.e. $K = \text{Vapor Press of Pure Liquid}$

$$= P_{A, \text{vap}}$$

so $(P_A)_{eq} = X_{A(l)} P_{A, \text{vap}}$ Raoult's Law

Name of
equation??

**Van't
Hoff**

VAPOR PRESSURE VS. T For H₂O

$$\text{GIVEN: } (P_{\text{H}_2\text{O}})_{\text{eq}} \text{ AT } 373 \text{ K} = 1.00 \text{ atm}$$

$$\epsilon \cdot \Delta H_{\text{vap}}^{\circ} = 40,600 \text{ J/mol } \ddagger \text{ Constant}$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \text{ for } \underline{\text{all}} \text{ reactions}$$

For H₂O(l, pure) → H₂O(gas)

$$K = (P_{\text{H}_2\text{O}})_{\text{eq}} = \text{Vapor Pressure.}$$

$$\ln \frac{P_{298}}{P_{373}} = -\frac{\Delta H_{\text{vap}}^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{P_{298}}{1} = -\frac{40600}{8.3145} \left(\frac{1}{298} - \frac{1}{373} \right)$$

$$= -3.41$$

$$P_{298} = e^{-3.41} = 0.033 \text{ atm}$$

actually it is 0.032

In BOZEMAN $P_{\text{atm}} = 0.83 \text{ atm}$

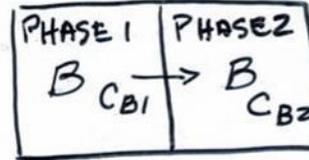
$$\text{Boiling Point? } \ln 0.83 = -\frac{40600}{8.3145} \left(\frac{1}{T_{\text{b.p.}}} - \frac{1}{373} \right)$$

$$T_{\text{bp}} = 368 \text{ K} = 95^{\circ}\text{C}$$

Knowing
LeChatelier
means never
getting the sign
wrong.

boiling point will be
temperature when
vapor pressure=0.83

SOLUTE TRANSFERS



$C_B =$ Either $[B]$ OR X_B

A = solvent B = SOLUTE

PHASE 1	PHASE 2	$\frac{Q}{Q^0} = \frac{a_{B2}}{a_{B1}} / \frac{Q^0}{Q^0}$	ΔM^0	$K = e^{-\frac{\Delta M^0}{RT}}$	Chap. 5 HOMEWORK PROBS.
Liquid A	Liquid A + FIELD	$\frac{\gamma_2 C_{B2}}{\gamma_1 C_{B1}}$	0 also $\Delta H^0 = 0$	1	
Liquid A	Liquid A'	$\frac{\gamma_2 C_{B2}}{\gamma_1 C_{B1}}$	$\neq 0$	Partition Coefficient	
Pure Solid B	Liquid A	$\frac{\gamma_2 C_B}{1}$	$\neq 0$	Solubility $= \gamma_2 C_{B eq}$	
Liquid A	GAS	$\frac{P_B}{\gamma_1 X_B}$ or $\frac{P_B}{\gamma_1 [B]}$	$\neq 0$ $\Delta H^0 = +$ ALWAYS	HENRY'S LAW $\propto \frac{1}{\text{Solubility of gas in liquid}}$	

Vap Press of gas B ALWAYS increases as T increases

so, Solubility of gas in liquid ALWAYS decreases as temperature increases

$$\ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = -\frac{\Delta H^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Henry's Law K:

$$K = \frac{\text{Vap. Pressure}}{\text{Solubility}}$$

HENRY'S LAW CONSTANT

is a partition coefficient, i.e., an **equilibrium constant**

$$K = \frac{\text{partial pressure of gas}}{\text{concentration of dissolved gas}} = \frac{p_B}{[B]} \quad \text{or} \quad \frac{p_B}{x_B}$$

OR

$$K = \frac{\text{concentration of dissolved gas}}{\text{partial pressure of gas}} = \frac{[B]}{p_B} \quad \text{or} \quad \frac{x_B}{p_B}$$

4 possibilities: forward or backward with x or p
you tell which by the **UNITS of the Henry's Law Constant**

All of the above are Henry's Law

Solute Transfer. Solute = B



always $\Delta G = \Delta G^\circ + RT \ln \left(\frac{a_2}{a_1}\right)^Q$

Case 4 B(in solvent) \longrightarrow B(gas) Henry's Law



Two Conventions $Q \equiv \frac{P_{B(\text{gas})}}{[B(\text{aq})]}$ or, $\frac{P_{B(\text{gas})}}{X_{B(\text{aq})}}$

Therefore $K^M = \left(\frac{P_B}{[B(\text{aq})]}\right)_{\text{eq}}$ or $K^X = \left(\frac{P_B}{X_B}\right)_{\text{eq}}$ Table 5.1

Henry's Law

$P_B = K^M [B]$ or $K^X X_B$: Vapor Press. of a dissolved gas is proportional to Conc

or $[B]_{\text{eq}} = \frac{P_B}{K^M}$ or $X_B = \frac{P_B}{K^X}$ Solubility is proportional to $\frac{1}{P_B}$

What is Q?

What is K?

Multiply by Conc.
Looks exactly like
Raoult's Law:

$$P_B = X_B K^X$$

Divide by K:

Concentration of gas
is proportional to P_B

TABLE 6.1 Henry's Law coefficients $k_B = p_{v,B}/x_B$, in bar, for aqueous solutions

Gas	0°C	25°C	37°C
He	131×10^3	139×10^3	138×10^3
N ₂	50×10^3	84×10^3	98×10^3
CO	35×10^3	57×10^3	67×10^3
O ₂	26×10^3	42×10^3	50×10^3
CH ₄	23×10^3	38×10^3	46×10^3
Ar	24×10^3	38×10^3	45×10^3
CO ₂	0.71×10^3	1.59×10^3	2.13×10^3
C ₂ H ₂	0.71×10^3	1.32×10^3	1.69×10^3

Source: Based on data from Harvey, A. H., "Semiempirical correlation for Henry's constants over large temperature ranges," *AIChE Journal*, 42, pp. 1491–1494. DOI: 10.1002/aic.690420531. Copyright (c) 1966 John Wiley and Sons, Inc.

What STRIKES you about this table? Huge numbers; always increase with T

Why do they always increase with increasing temperature?

The units are bars per mole fraction;

What is the chemical equation for the process here?

Why are the constants so large?

$$k_B = K_{eq} = \frac{\text{Vapor Pressure of dissolved gas}}{\text{Solubility of dissolved gas}}$$

$$k_B = K_{eq} = \frac{\text{equilibrium partial pressure of gas above liquid}}{\text{equilibrium concentration of dissolved gas}}$$

Always the same proportion

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Why are they so large???

They are the equilibrium pressure of the "pure dissolved gas" i.e. $X_{\text{gas}} = 1$
Hypothetical standard state of pure aqueous gas with a $\Delta H^0 =$ to that of the gas surrounded by the solvent.

The numbers are straight-line EXTRAPOLATIONS of values at very low mole fraction up to $X = 1$ for the dissolved gas.

Let's talk about bubbles

$$K = [B(aq)] / p_B \quad (\text{a form of Henry's Law})$$

What happens if equilibrium is reached with **HIGH PRESSURE** and then pressure is reduced quickly?

Name 2 phenomena associated with this?

1. Opening a carbonated drink.
2. Diver coming to surface too quickly

What happens if equilibrium is reached with **LOW TEMPERATURE** and then temperature is raised quickly?

Bubbles of AIR form. Crucial to boiling.

Partition Coefficients

Most common: $B(\text{solvent 1}) \rightarrow B(\text{solvent 2})$ $K_{\text{eq}} = [B(2)]/[B(1)]$

e.g., using “sep funnel”

More generally: for A solvent B solute

<u>Name</u>		<u>Partition Coef (K_{eq})</u>
Henry's Law constant	$B(\text{solvent}) \leftrightarrow \text{gas}(\text{vacuum})$	$P_B/[B]$ or P_B/X_B
Evaporation/Condensing	$A(\text{liquid}) \leftrightarrow \text{gas}(\text{vacuum})$	$P_A/X_A = \text{Vapor Press}$
Dissolving/Crystallizing (solubility)	$\text{crystal} \leftrightarrow \text{any solvent}$	e.g., $[B(\text{aq})]/1$
Melting/freezing	$A(\text{s}) \leftrightarrow A(\text{liquid})$	$X_A/1$