

# Physical Chemistry

## Lecture 33

### Henry's Law, Solute Activity, and the Practical Osmotic Coefficient

## Dilute solutions and Henry's law

- ◆ Gases dissolve in liquids to form dilute solutions
- ◆ First investigated by Henry
- ◆ Henry's law relates the solution concentration to the equilibrium pressure
- ◆ Only an approximate "law"
- ◆ Henry's-law constants defined in the limit

$$P_i = k_X X_i$$

$$P_i = k_m m_i$$

$$P_i = k_c c_i$$

$$k_X = \lim_{X \rightarrow 0} \frac{P_i}{X_i}$$

$$k_m = \lim_{m \rightarrow 0} \frac{P_i}{m_i}$$

$$k_c = \lim_{c \rightarrow 0} \frac{P_i}{c_i}$$

## Gas solubilities at 298.15 K and 1 atmosphere

- ◆ Used to determine Henry's-law constant
- ◆ Solubility depends on both the solute and the solvent
- ◆ Amount dissolved is very small
  - Dilute-solution limit

Gas	Solvent	$X_2$
Argon	Benzene	$8.77 \times 10^{-4}$
Argon	n-Hexane	$2.53 \times 10^{-3}$
Argon	Water	$2.7 \times 10^{-5}$
Carbon dioxide	Water	$6.1 \times 10^{-4}$
Nitrogen	Water	$1.2 \times 10^{-5}$
Oxygen	Water	$2.3 \times 10^{-5}$

## Henry's law and real solutions

- ◆ Activity is determined by Henry-law relation
- ◆ Activity of 1 determines the standard state
  - Usually at unit concentration
- ◆ Pressure at the standard state is determined by the Henry-law constant
- ◆ Ideal system has an activity coefficient of 1 for all conditions

$$P_i = k_i a_{i,liq}^{HL}$$

$$a_{i,liq}^{HL} = \gamma_{im} m_i$$

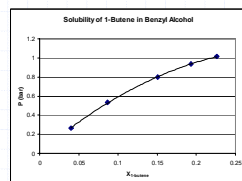
$$a_{i,liq}^{HL} = \gamma_{iX} X_i$$

$$a_{i,liq}^{HL} = \gamma_{ic} c_i$$

## Solubility data and Henry's law

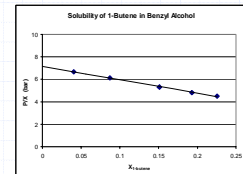
- ◆ Example: 1-butene in benzyl alcohol at 0°C
- ◆ Solubility is **NOT** linear in the pressure, as expected from Henry's law
- ◆ Find Henry-law constant as a limiting value

Pressure/torr	$X_{1\text{-butene}}$
200	0.040
400	0.087
600	0.151
700	0.193
760	0.226



## Finding the Henry-law constant as a limiting value of solubility

- ◆ Example: 1-butene in benzyl alcohol at 0°C
- ◆ Plot  $P/X$  versus  $X$  and extrapolate to  $X = 0$
- ◆  $k_X = 7.14$  bar



$$k_X = \lim_{X \rightarrow 0} \frac{P}{X}$$

## Activities and activity coefficients on the Henry-law scale

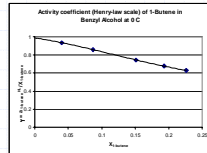
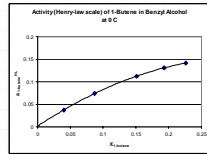
◆ Example: 1-butene in benzyl alcohol at 0°C

◆ Activity is defined as

$$a_i^{HL} = \frac{P_i}{k_{HL}}$$

◆ Activity coefficient is defined as

$$\gamma_i^{HL} = \frac{a_i^{HL}}{X_i}$$



## Relation of activities of the solute and the solvent

- ◆ Must find ways to measure activities of substances that do not have high vapor pressures
- ◆ Raoult's law and Henry's law are not appropriate
- ◆ Activities of the two components are related by the Gibbs-Duhem equation

$$n_1 d\mu_1 = -n_2 d\mu_2$$

- ◆ Allows determination of activity of one substance from that of the other

$$d \ln a_2 = -\frac{n_1}{n_2} d \ln a_1$$

## Practical osmotic coefficient

◆ Define the activities of both components in terms of a single parameter,  $\phi$

$$\phi(m) = -\left(\frac{1000}{M_1 m}\right) \ln a_1$$

◆ With this definition, solute activity coefficient is an integral

$$\ln \gamma_{2,m}(m) = \phi(m) - 1 + \int_0^m \frac{\phi(m') - 1}{m'} dm'$$

◆ Prediction of the concentration dependence of  $\phi$  gives all the information about a solution

## Summary

- ◆ Henry's law is derived from solubility measurements
- ◆ Henry-law standard state – the molecule (at unit concentration) surrounded by unlike molecules
- ◆ Activity determined relative to ideal Henry-law predictions of pressure
- ◆ Activities of both components are related
- ◆ Gibbs-Duhem relation gives ability to determine activity of one component from that of the other