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 William Henry in 1803
- Henry's law relates the solution concentration the equilibrium pressure

$$P_i = k_X X_i$$

$$P_i = k_m m_i$$

$$P_i = k_c c_i$$

Dilute solutions and Henry’s law

- Gases dissolve in liquids to form dilute solutions
- First investigated by William Henry in 1803
- Henry’s law relates the solution concentration the equilibrium pressure
- Only an approximate “law”
- Henry’s-law constants defined in the limit

$$P_i = k_X X_i$$

$$P_i = k_m m_i$$

$$P_i = k_c c_i$$

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

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

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

Gas solubilities at 298.15 K and 1 atmosphere

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

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

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

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

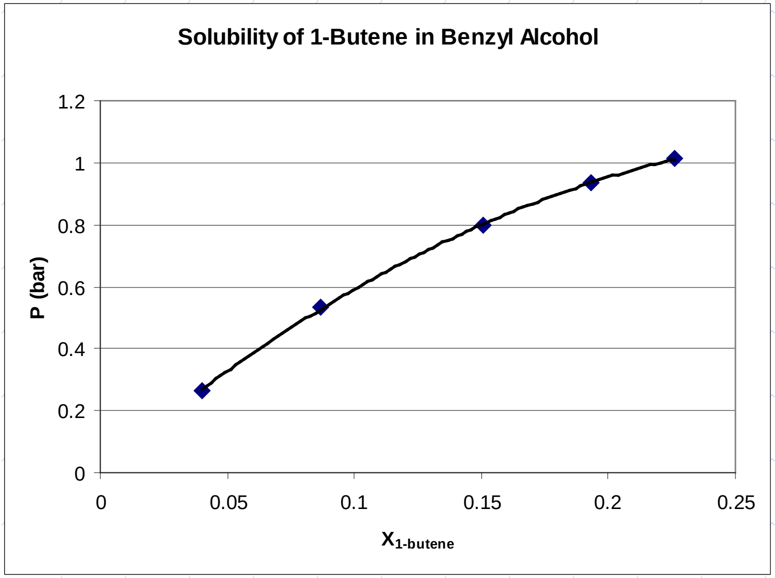
$$a_{i,liq}^{HL} = \gamma_{iX} X_i$$

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

Solubility data and Henry's law

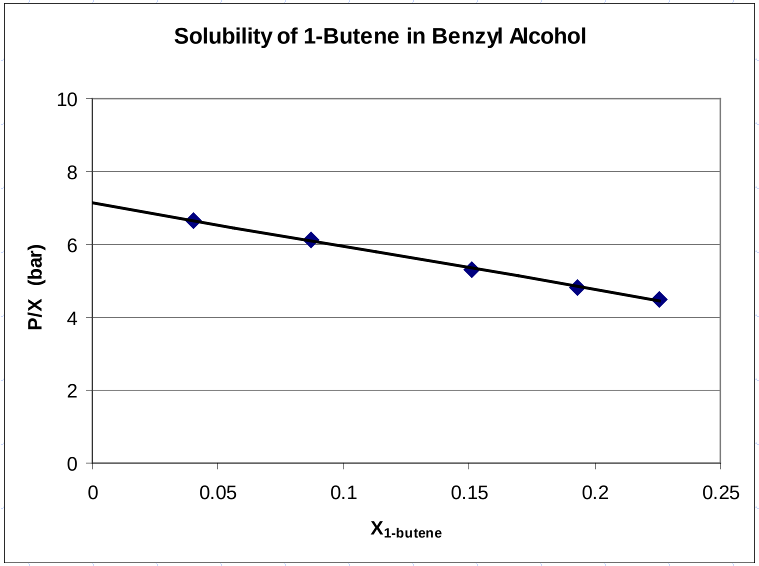
- Example: 1-butene in benzyl alcohol at 0°C
- Solubility is NOT linear in the pressure, as expected from Henry's law
- Find Henry-law constant as a limiting value

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



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

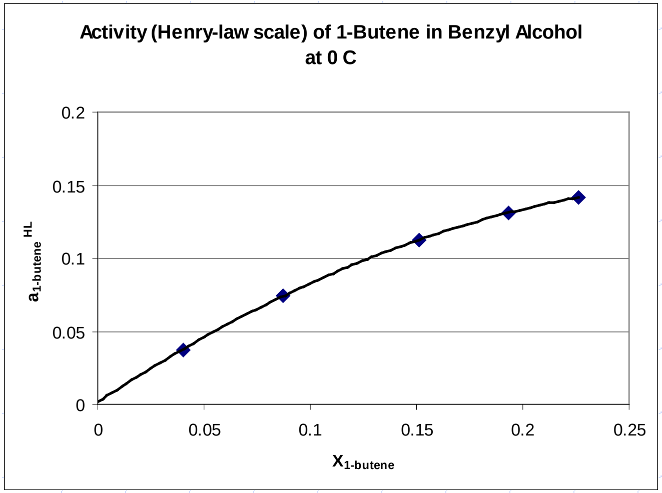
Activities and activity coefficients on the Henry-law scale

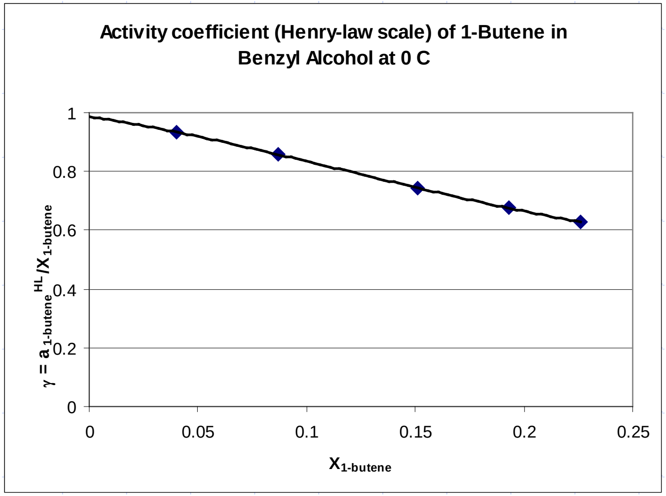
- Example: 1-butene in benzyl alcohol at 0°C
- Activity is defined as

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

- 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, *Φ*, the osmotic coefficient

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

- Solute activity coefficient determined by an integral of the osmotic coefficient

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

- Prediction of the concentration dependence of Φ 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