Lindane Solubility

- The chemical formula for lindane is $C_6H_6Cl_6$, and it has a molecular weight of 290.83
- Lindane is a white crystalline solid that is volatile in air and insoluble in water. (1)
- Lindane vapor is colorless and has a slight musty odor; the odor threshold is 12 par

- EPA considers lindane to be a possible human carcinogen (cancer-causing agent) and has ranked it in EPA's Group B2/C. (6)
- EPA has established an oral cancer slope factor of 1.3 (mg/kg/d)$^{-1}$. (6)
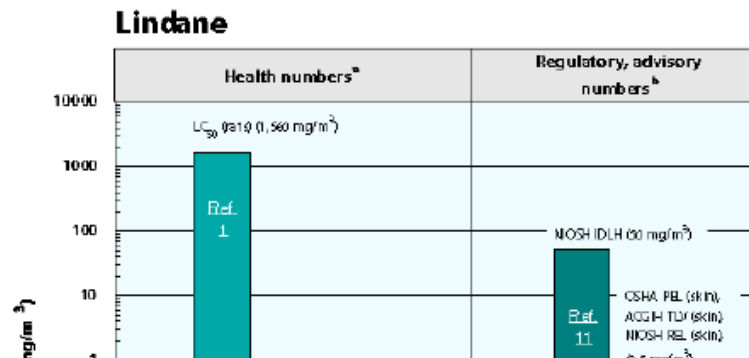- CalEPA has calculated an inhalation unit risk factor of 3.1 x 10^{-4} (µg/m^3)$^{-1}$. (8)

Physical Properties

- Lindane is the common name for gamma-hexachlorocyclohexane. (1,5)
- The chemical formula for lindane is $C_6H_6Cl_6$, and it has a molecular weight of 290.83 g/mol. (1)
- Lindane is a white crystalline solid that is volatile in air and insoluble in water. (1)
- Lindane vapor is colorless and has a slight musty odor; the odor threshold is 12 parts per million (ppm). (1)
- The vapor pressure for lindane is 9.4 × 10^{-6} mm Hg at 20 °C, and it has a log octanol/water partition coefficient (log K_{ow}) of 3.3. (1)

Conversion Factors:
To convert concentrations in air (at 25 °C) from ppm to mg/m^3: mg/m^3 = (ppm) × (molecular weight of the compound)/(24.45). For lindane: 1 ppm = 11.89 mg/m^3. To convert concentrations in air from µg/m^3 to mg/m^3: mg/m^3 = (µg/m^3) × (1 mg/1,000 µg).

Health Data from Inhalation Exposure

Lindane

	Health numbers^a	Regulatory, advisory numbers^b
10000		
1000	LC$_{50}$ (rat) (1,560 mg/m^3) Ref. 1	
100		NIOSH IDLH (50 mg/m^3)
10		OSHA PEL (skin), ACGIH TLV (skin), NIOSH REL (skin) Ref. 11
1		

Lindane Solubility

Abstract   Figures

Full Text HTML   Citing Articles

Hi-Res PDF [166 KB]

PDF w/ Links [284 KB]

Lindane solubility = 7.3 mg/L

Lindane MCL = 0.0002 mg/L

36,500-fold difference!!
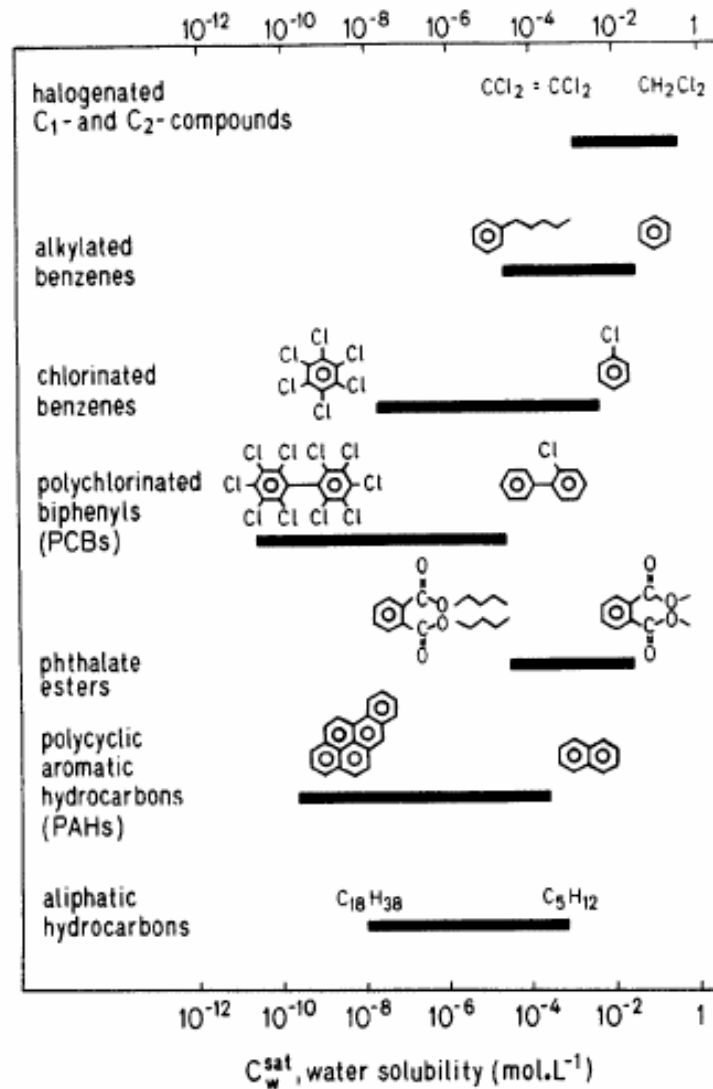
Huge range aq. Solubilities!

Figure 5.1 Ranges in water solubilities (C_w^{sat}) of some important classes of organic compounds.

# Mole fraction of organic liquids that are saturated with water: $x^o_{i,L}$

TABLE 5.1   Mole Fraction of Some Common Nonpolar Organic Liquids Saturated with Water

Organic Liquid	x_o	Reference
Pentane	0.99952	
Hexane	0.99946	
Heptane	0.99916	Gerrard, 1980
Octane	0.99911	
Benzene	0.9977	
Chlorobenzene	0.9975	
1,2,-Dichlorobenzene	0.9973	
1,2,4-Trichlorobenzene	0.9980	
Trichloroethylene	0.9977	Horvath, 1982
Tetrachloroethylene	0.99913	
Methylene chloride	0.9914	
Chloroform	0.9946	
1,1,1-Trichloroethane	0.9974	
Diethyl ether	0.942	
Butyl acetate	0.89	
Methyl acetate	0.74	Riddick and Bunger, 1970
2-Butanone	0.69	
3-Pentanone	0.89	
Pentanol	0.64	Stephenson et al., 1984
Octanol	0.79	

Aqueous Activity Coefficients

Compound	γ_{iw}^{∞}	$G_{iw}^{E,\infty\ b}$ (kJ·mol^{-1})
Methanol	1.6	1.2
Ethanol	3.7	3.2
Acetone	7.0	4.8
1-Butanol	5.0×10^1	9.7
Phenol	5.7×10^1	10.0
Aniline	1.3×10^2	12.1
3-Methylphenol	2.3×10^1	13.5
1-Hexanol	8.0×10^2	16.5
Trichloromethane	8.2×10^2	16.6
Benzene	2.5×10^3	19.4
Chlorobenzene	1.3×10^4	23.5
Tetrachloroethene	5.0×10^4	26.8
Naphthalene	6.9×10^4	27.6
1,2-Dichlorobenzene	6.8×10^4	27.6
1,3,5-Trimethylbenzene	1.2×10^5	29.0
Phenanthrene	1.7×10^6	35.5
Anthracene	2.7×10^6	36.7
Hexachlorobenzene	3.5×10^7	43.0
2,4,4'-Trichlorobiphenyl	4.7×10^7	43.8
2,2',5,5'-Tetrachlorobiphenyl	7.5×10^7	44.9
Benzo(a)pyrene	2.7×10^8	48.1

Thermodynamics of Dissolution

HIGH energy
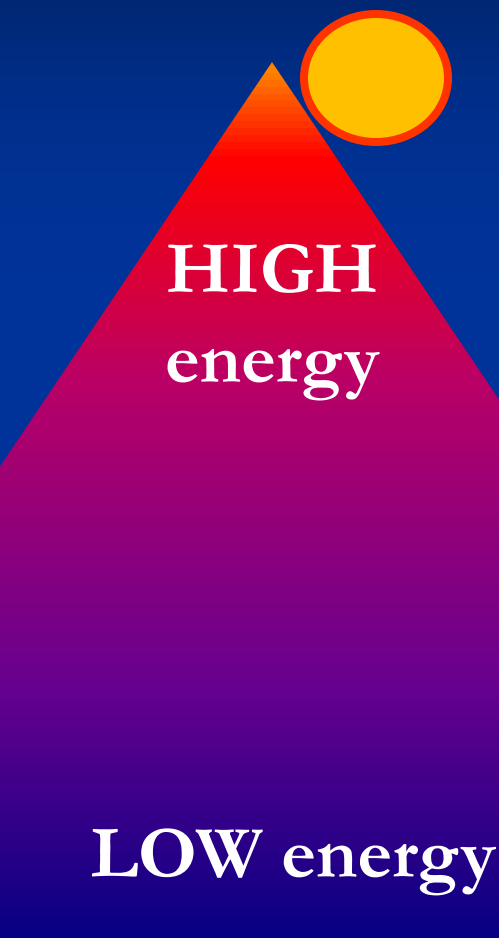
LOW energy
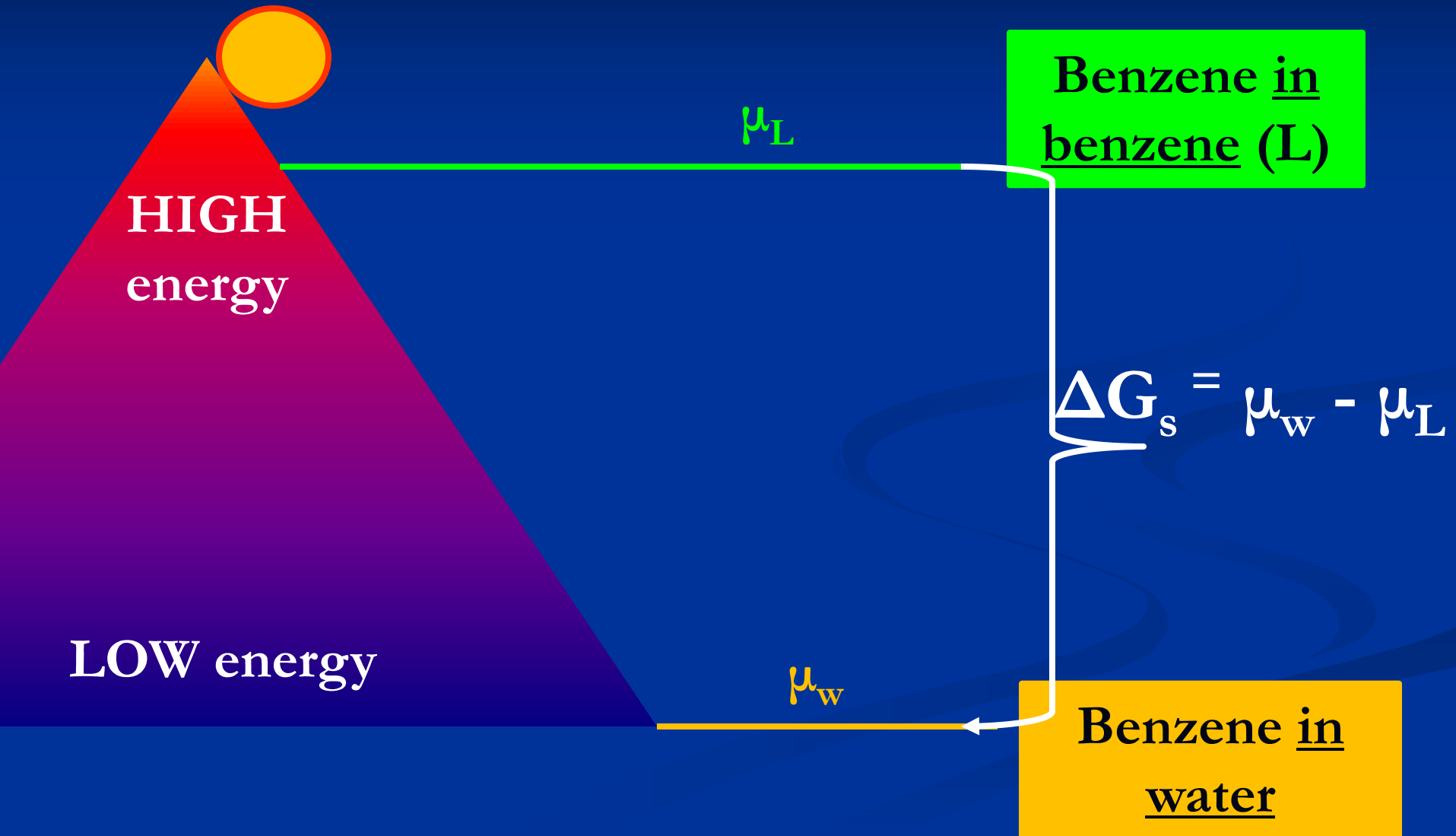
Reactions occur because they are energetically favorable → they proceed from **HIGH** to **LOW** energy

if $\Delta G_{sol} < 0$, the rxn is spontaneous

When water is "saturated" system is at EQ

$\Delta G = 0$

Thermodynamics of Dissolving Benzene

μ_L

Benzene <u>in</u> <u>benzene</u> (L)

HIGH energy

$\Delta G_s = \mu_w - \mu_L$

LOW energy

μ_w

Benzene <u>in</u> <u>water</u>
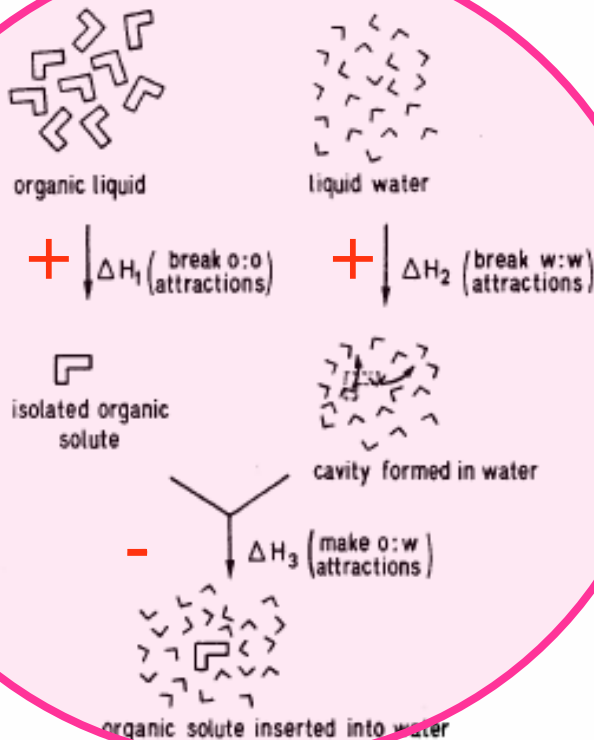
Huge range in solubility & activity coefficient
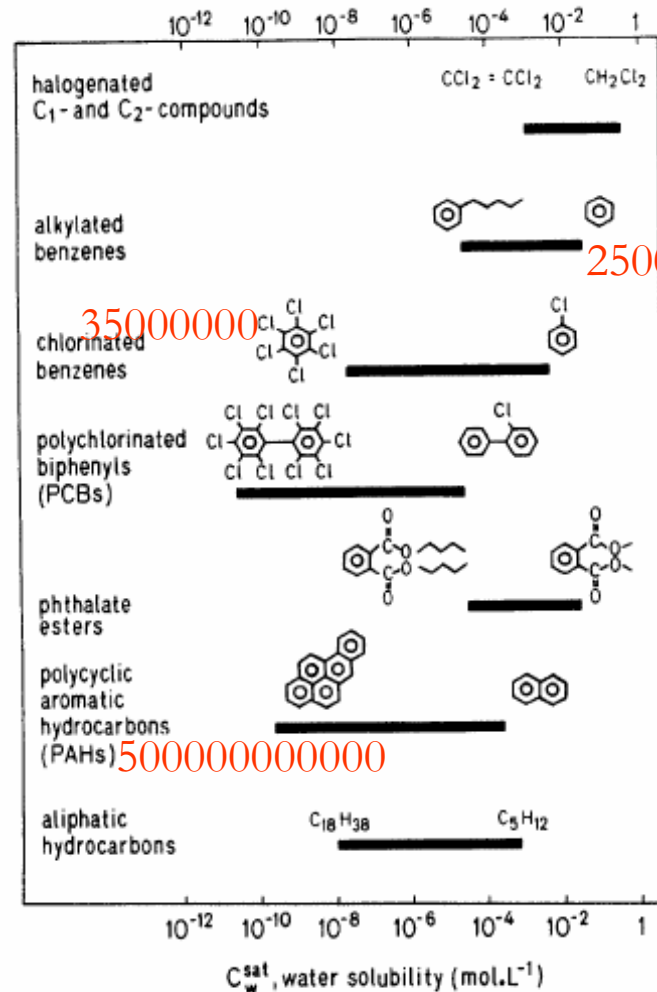
Figure 5.1 Ranges in water solubilities (C_w^{sat}) of some important classes of organic compounds.

Molecular View & Enthalpy

Cavity
filling

"Ice"

formation

Figure 5.2 Schematic representation of the various enthalpies involved when dissolving a

$$o:o + w:w \rightarrow w:o:w$$

Ideal Mixing

$$\Delta H_1 + \Delta H_2 = -\Delta H_3$$
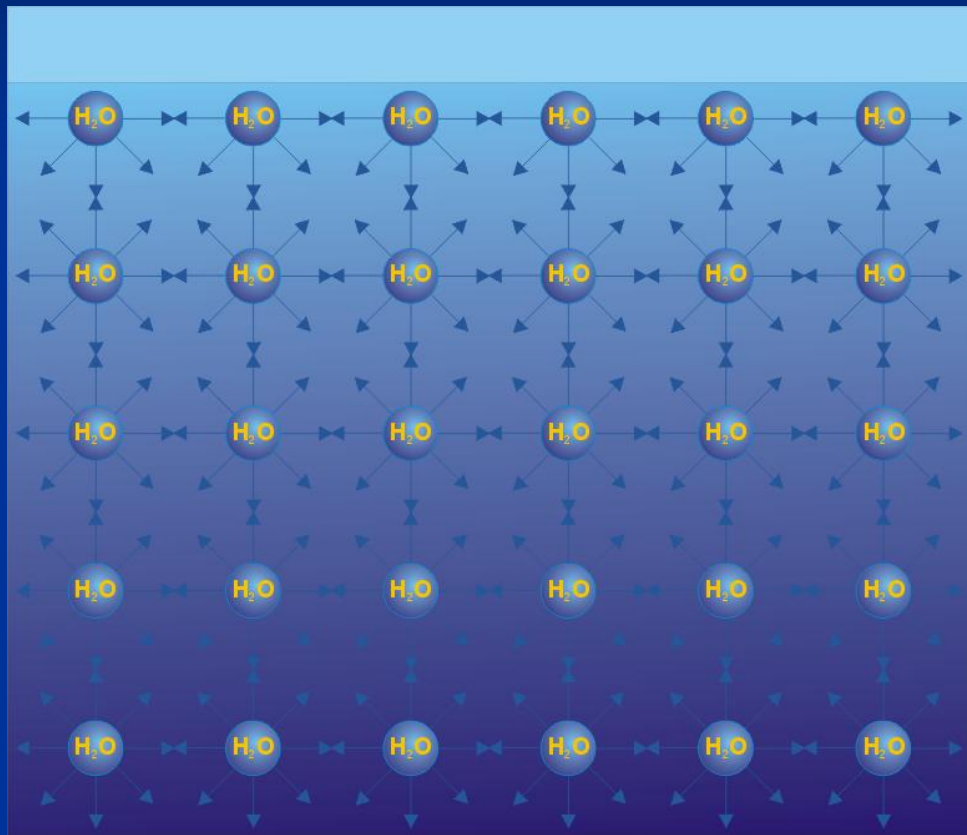
So…

$$\sum \Delta H_{1,2,3} = \Delta H^E_{diss} = 0$$

Nonideal "excess"

$$\sum \Delta H^E_{1,2,3,4} = \Delta H^E_{diss} = > 0$$

$$|\Delta H_1 + \Delta H_2| > |\Delta H_3 + \Delta H_4|$$

$$\Delta H^E_{diss} > 0 \text{ (nonpolars)}$$

net loss of Hbonds in exchange
for weaker intermolecular forces

Forming a cavity requires "breaking" water's Hbonds

cavity
cavity-lining water

bulk water

Molecular View & Enthalpy
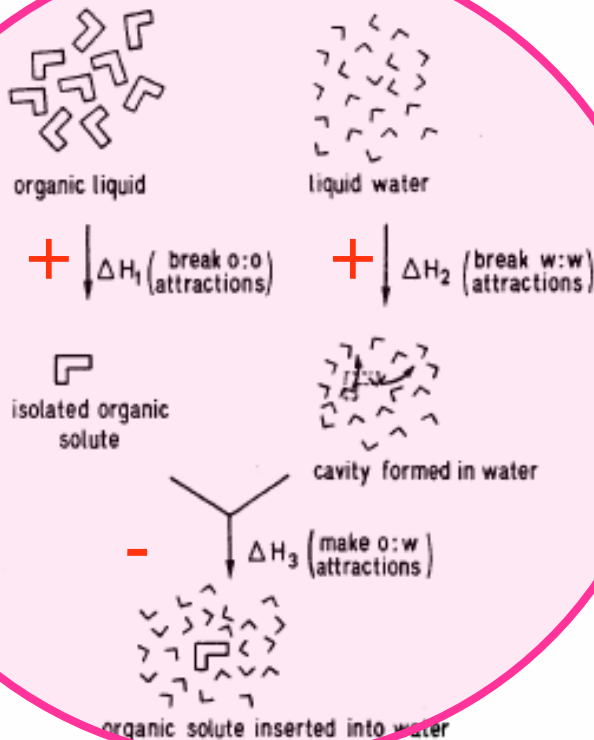
Cavity filling

"Ice" formation

Figure 5.2 Schematic representation of the various enthalpies involved when dissolving a

o:o + w:w → w:o:w

Ideal Mixing

$\Delta H_1 + \Delta H_2 = -\Delta H_3$

So…
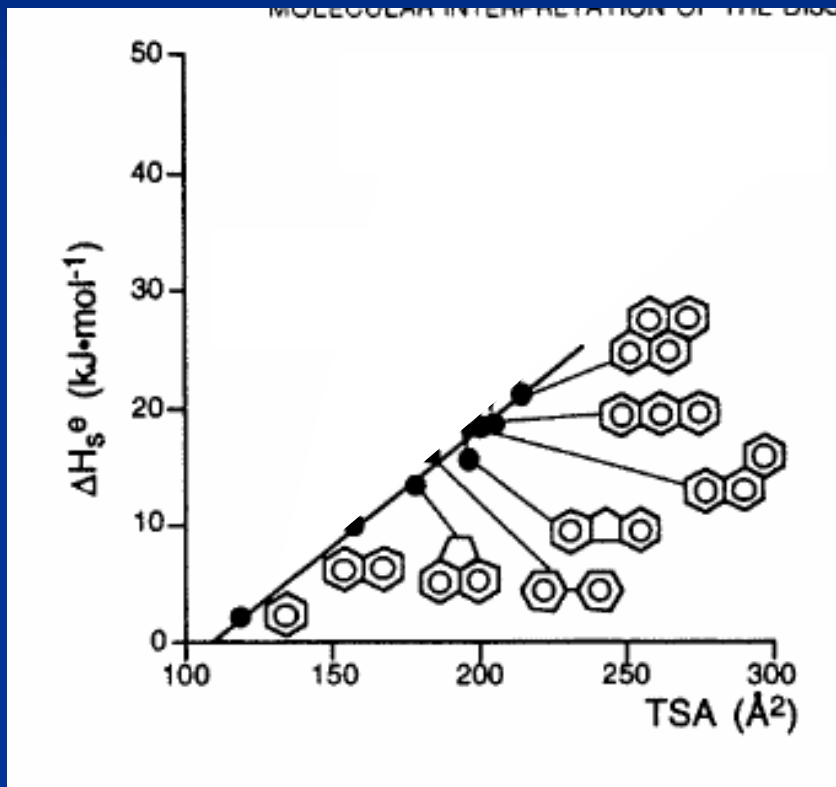
$\sum \Delta H_{1,2,3} = \Delta H^E_{diss} = 0$

Nonideal "excess"

$\sum \Delta H^E_{1,2,3,4} = \Delta H^E_{diss} = > 0$

$|\Delta H_1 + \Delta H_2| > |\Delta H_3 + \Delta H_4|$

$\Delta H^E_{diss} > 0$ **(nonpolars)**

net loss of Hbonds in exchange for weaker intermolecular forces

Positive Excess ΔH limits solubility

Due to <u>net loss</u> of water's H-bonds in exchange for weaker forces of attraction

Magnitude is

- Related to solute (& hence, cavity) size
- Solute Polarity/polarizability

Molecular View & Entropy

Cavity Filling

organic liquid

liquid water

ΔH_1 (break o:o attractions)

ΔH_2 (break w:w attractions)

isolated organic solute

cavity formed in water

ΔH_3 (make o:w attractions)

organic solute inserted into water

ΔH_4 (strengthen w:w attractions as waters lining cavity re-orient to form flickering crystal)   "Ice"

formation

water molecules on edge of cavity orient

Figure 5.2 Schematic representation of the various enthalpies involved when dissolving a

o:o + w:w → w:o:w

$\Delta S_{mixing} > 0$
Mixing increases chaos!
Chaos is good for spontaneity!!
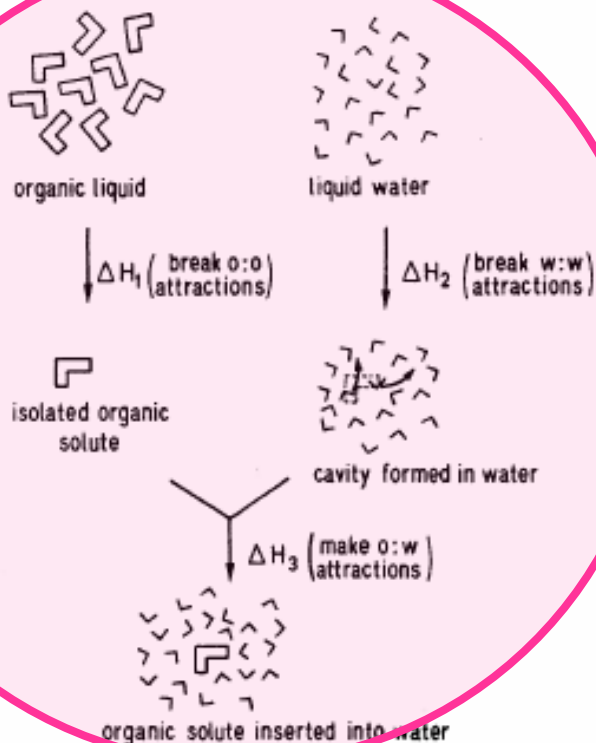
Non-Ideal "excess"
$\sum \Delta S^E_{1,2,3,4} < 0$

Solute trapping in "ice" cavity limits solubility!

Negative Excess ΔS limits solubility

C#-alcohol (OH)	$-T\Delta S^E$ (kJ/mol)
C1-OH	8.7
C2-OH	13.1
C3-OH	15.1
C4-OH	19.3
C6-OH	20.3
C8-OH	22.6
C12-OH	27.3

Due to <u>net loss</u> of solute's disorder/chaos/freedom

Magnitude is related to solute's "initial" freedom in its own pure phase

…. not size alone

Negative Excess Entropy limits solubility
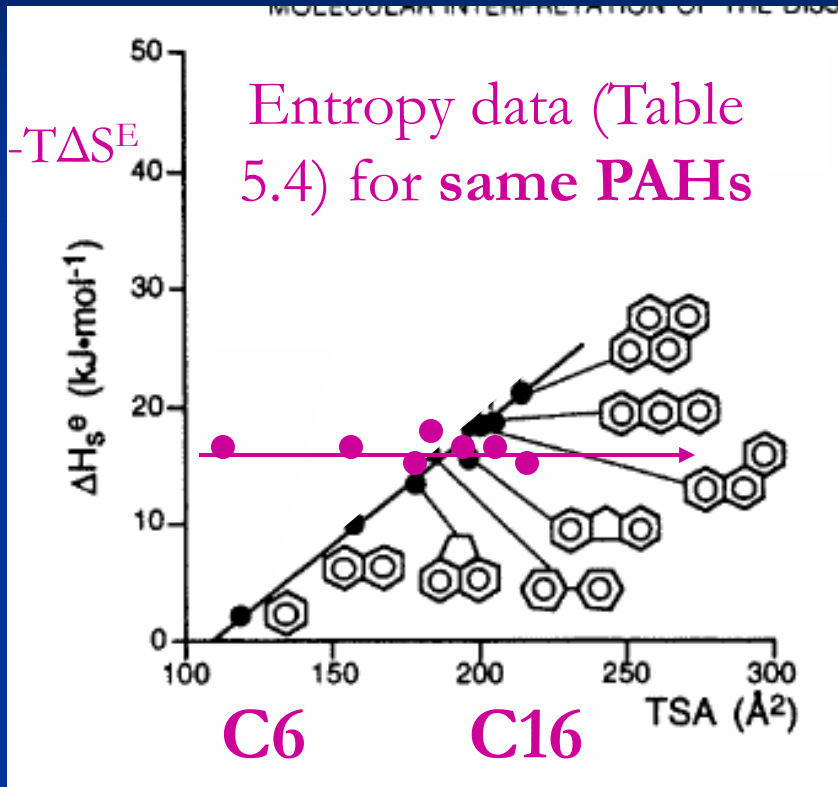
Entropy data (Table 5.4) for **same PAHs**

$-T\Delta S^E$

$\Delta H_s^\ominus$ (kJ·mol^{-1})

TSA (Å^2)

C6   C16

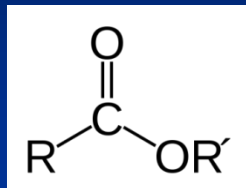Due to <u>net loss</u> of solute's disorder/chaos/freedom

Magnitude is related to
- solute's "initial" freedom in its own pure phase
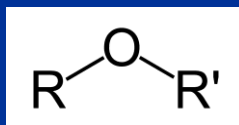 - Shape/flexibility (rings have less freedom; longer chains have more freedom)

Qualitative Solubility
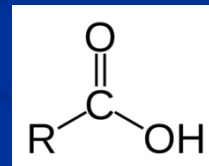
Highly polar groups

    -COO- (ester)

    -O-   (ether)

Polar groups

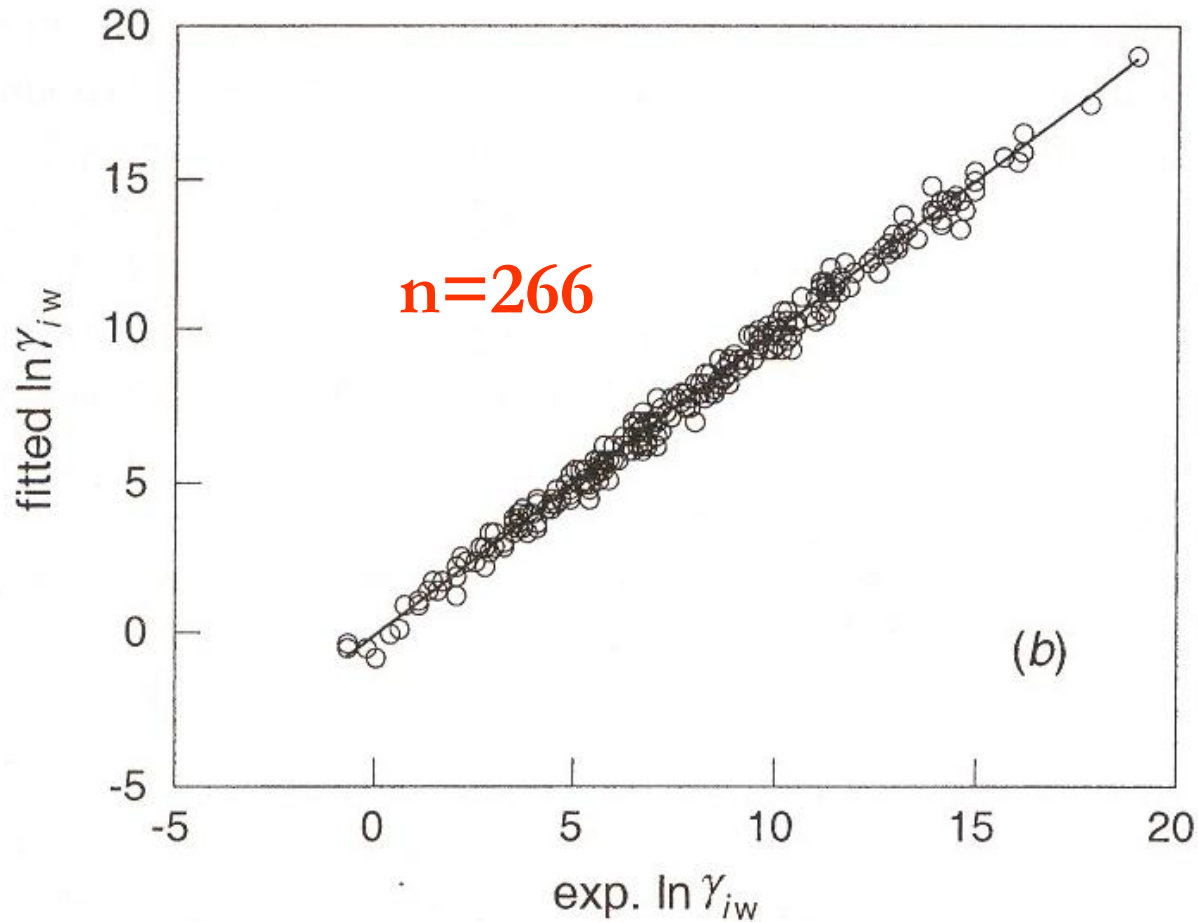   **-OH** (alcohol, "phenol" if its attached to benzene)

    -COOH (carboxylic acid)

    -NH$_2$ (amine)

Weakly polar: C-Cl, C-Br, C-H

γ Estimations vs Experiment

n=266

Activity coefficient estimation

$$\ln \gamma_{iw}^{sat} = -\ln p_{iL}^{\circ}(bar) - 0.572\left[(V_i)^{2/3}\left(\frac{n_{Di}^2 - 1}{n_{Di}^2 + 2}\right)\right] - 5.78\pi_i - 8.77(\alpha_i) - 11.1(\beta_i) + 0.0472V_i + 9.49$$

v.p. & LDF
p_{iL} = given or estimated
n_D = refractive index
(polarizability, Table 3.1)

Dipolarity & polarizability
π = "pi term"
(Table 5.5)

HDA interactions
H-donor (α) & H-acceptor (β) terms
(Table 4.3)

Volume term estimated

Solubility and Activity Coefficient Eqns.

$$C_{iw,L}^{sat}(mol/L) = \frac{1}{\overline{V}_w \gamma_{iw}^{sat}}$$

for liquids (& subcooled liquids)

$$C_{iw,S}^{sat}(mol/L) = \frac{1}{\overline{V}_w \gamma_{iw}^{sat}} e^{-\Delta_{fus}G_i / RT}$$

for solids,
where

$$\Delta_{fus}G_i(J/mol) = \left[56.5 + 9.2\tau - 19.2\log(\sigma)\right](T_m - T)$$

These equations tell us that all we need in order to estimate C_w^{sat} is an estimate/knowledge of

γ_{iw}^{sat}, τ, σ, and T_m
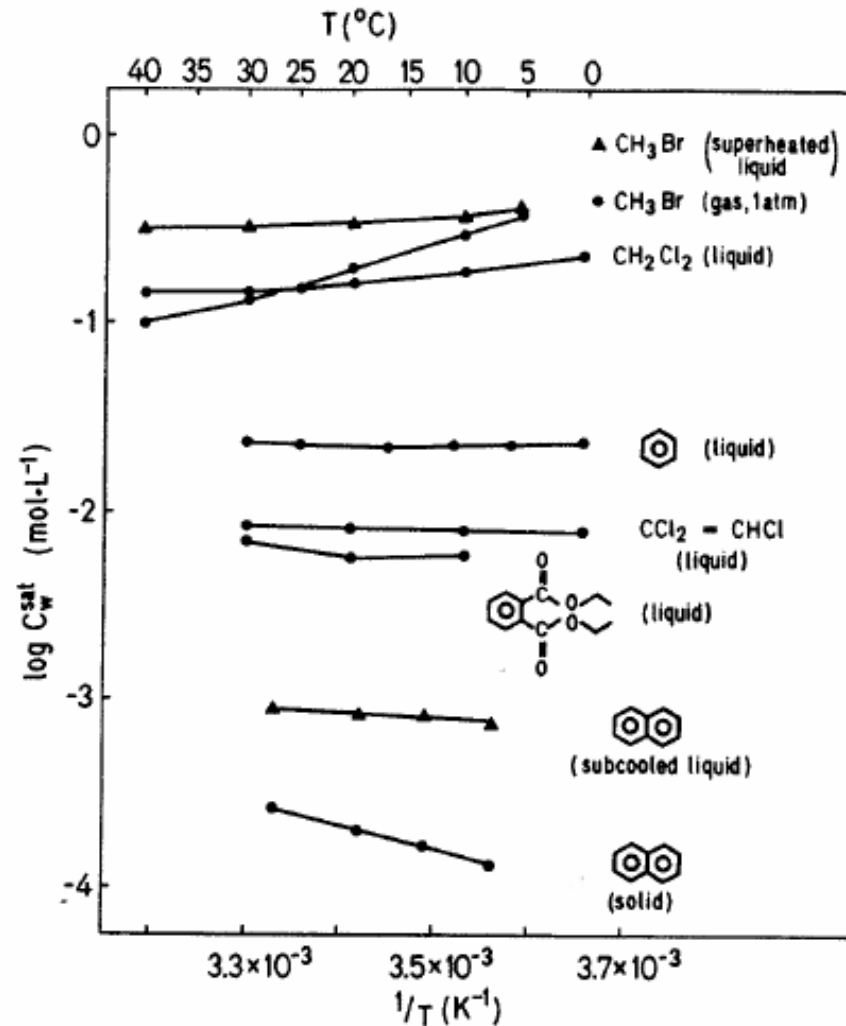
T-Solubility relationships

Figure 5.6 Solubility in water as a function of temperature for various compounds.
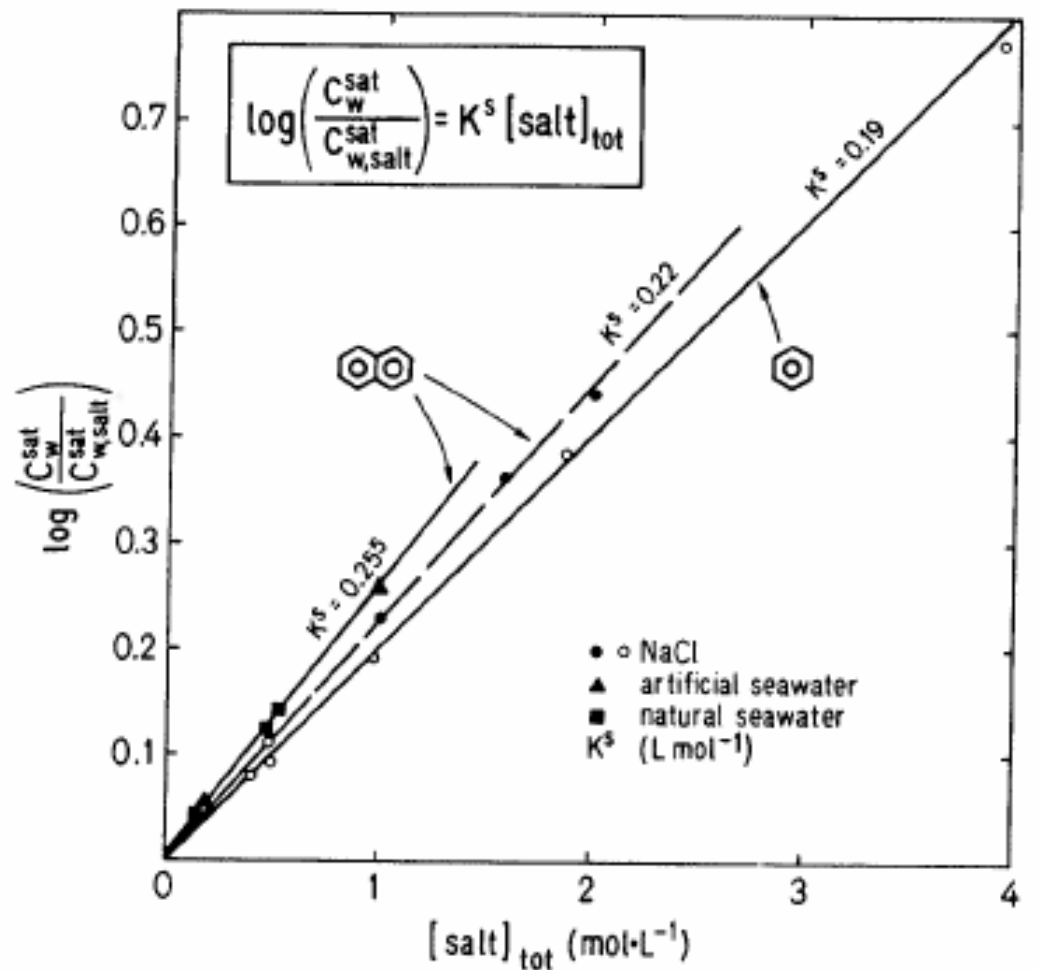
"Salting out"

Figure 5.7 Effect of salt concentrations on the aqueous solubility of benzene (McDevit and Long, 1952) and naphthalene (Gordon and Thorne, 1967a).