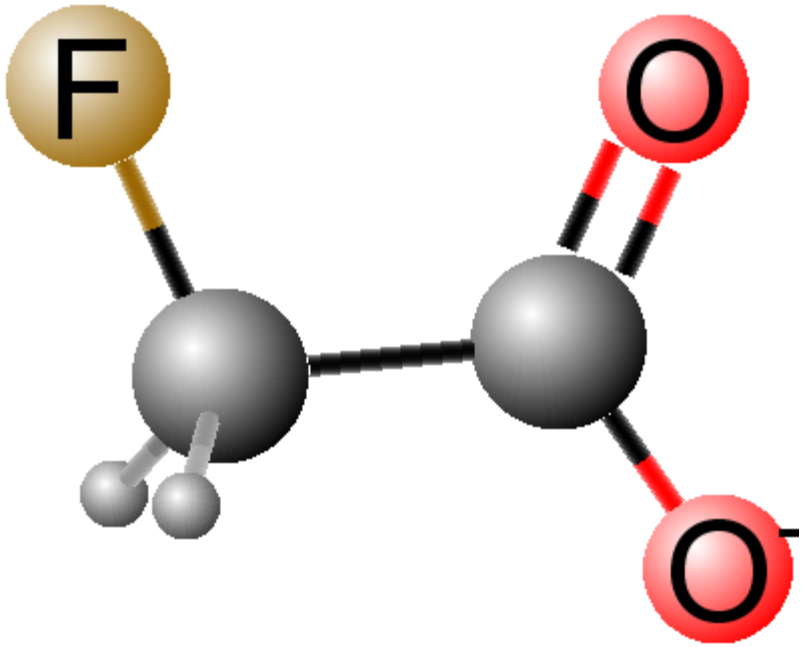
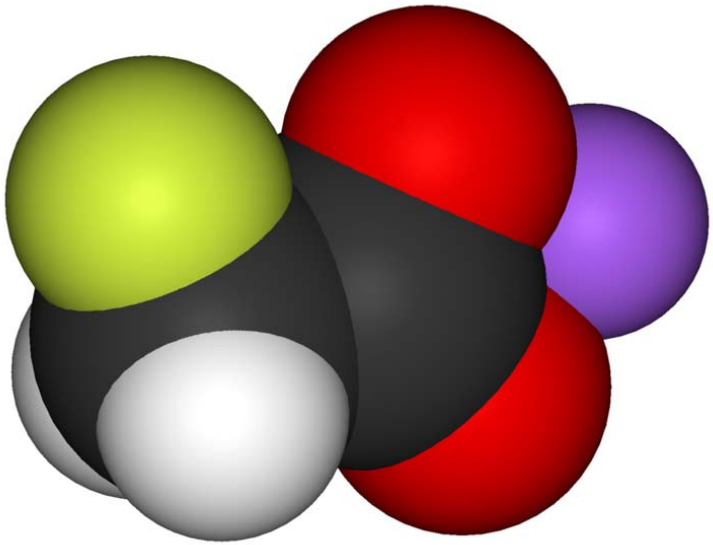
Interesting molecule of the day

- Sodium fluoroacetate

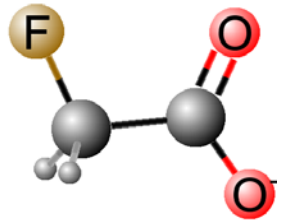




"Chailletia toxicaria“ to kill rats mice or coyotes!

Interesting molecule of the day

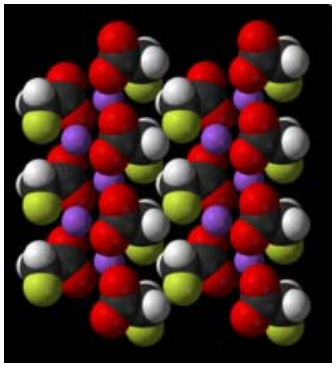
- sodium fluoroacetate (Compound 1080)



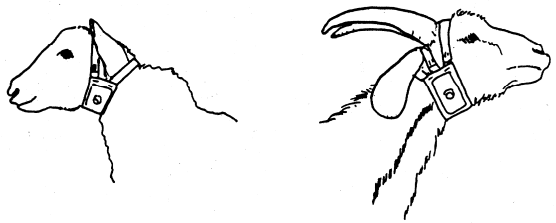
  - mw: 100.0 Da
  - T_m: 200°C
  - p_S* = 6.5x10^{-7} mm Hg
  - C_w^{sat}: miscible

  - toxicity
    - metabolic poison – disrupts the Krebs (citric acid) cycle
    - anti-herbivore (mammalian pests; invasive species)
    - lethal to humans at 2-10 mg kg^{-1} by ingestion
  - natural compound in 40 plants
    - e.g., *Dichapentalum cymosum*

Interesting molecule of the day



- EPA probes predator poisons sodium fluoroacetate and sodium cyanide (“M-44”)
  - released via gas canisters, livestock collars
  - USDA Wildlife Services
    - 14,000 coyotes, foxes, wolves killed in 2006
  - House bill introduced to ban compounds
  - EPA conducting environmental analysis



Interesting molecule of the day

Hunting deer in New Zealand

Aqueous Solubility

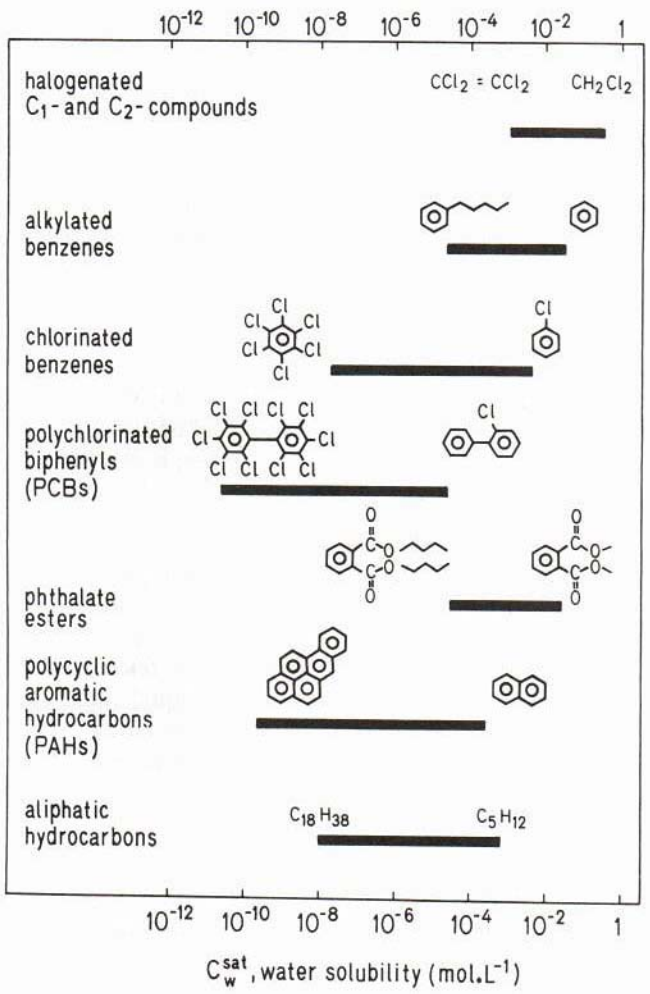


Figure 5.1 Ranges in water solubilities (C_w^{sat}) of some important classes of organic compounds.

$$C_w^{sat}$$

Environmentally relevant

<< 1 mol/L

Aqueous Solubility

- Another phase change
  - vapor pressure:
    - pure solid $\leftrightarrow$ gas (ideal)
    - pure liquid $\leftrightarrow$ gas (ideal)
  - aqueous solubility
    - pure solid $\leftrightarrow$ "liquid" in water (mixed, non-ideal)
    - pure liquid $\leftrightarrow$ liquid in water (mixed, non-ideal)
    - pure gas $\leftrightarrow$ "liquid" in water (mixed, non-ideal)
  - solubility (C_w^{sat}) at specified T and P

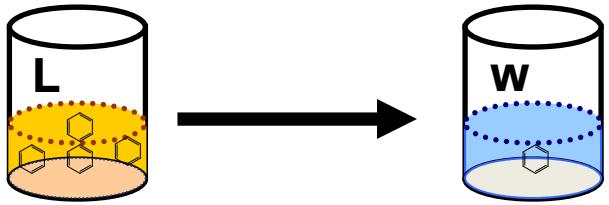
Aqueous Solubility

- What is the solubility of a Twinkie?

Aqueous Solubility

Aqueous Solubility

- Solubility of an organic liquid



$$\mu_L = \mu^0 + RT \ln \gamma_L x_L \qquad \mu_w = \mu^0 + RT \ln \gamma_w x_w$$

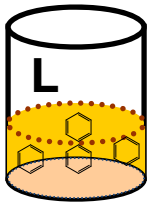
$$\Delta_w G = \mu_w - \mu_L$$

$$\Delta_w G = RT \ln \gamma_w x_w - RT \ln \gamma_L x_L$$

FREE ENERGY OF SOLUTION

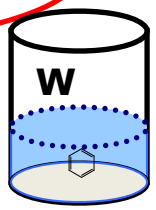
Aqueous Solubility

- Solubility of an organic liquid
  - assumptions about organic phase
    - $x_L \approx 1$ (essentially no water in organic phase)
    - $\gamma_L = 1$ (pure liquid; ideal interactions)



$$\Delta_w G = RT \ln \gamma_w x_w - \cancel{RT \ln(1)(1)}$$

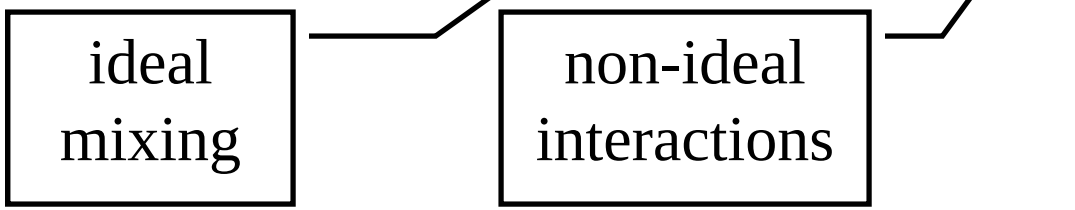
$$\Delta_w G = RT \ln \gamma_w x_w$$



Aqueous Solubility

- Solubility of an organic liquid
  - no melting
  - ideal mixing, $RT \ln x_w$
    - $\Delta_w S^{ideal}$ increases; change in molar volume
  - non-ideal interactions, $RT \ln \gamma_w$
    - enthalpy cost, $\Delta_w H^E$, and enthalpy cost, $\Delta_w S^E$
    - proportional to solute size $\Rightarrow$ cavity in water

$$\Delta_w G = RT \ln x_w + RT \ln \gamma_w$$



Aqueous Solubility

$$\Delta_w G = RT \ln x_w + RT \ln \gamma_w$$

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

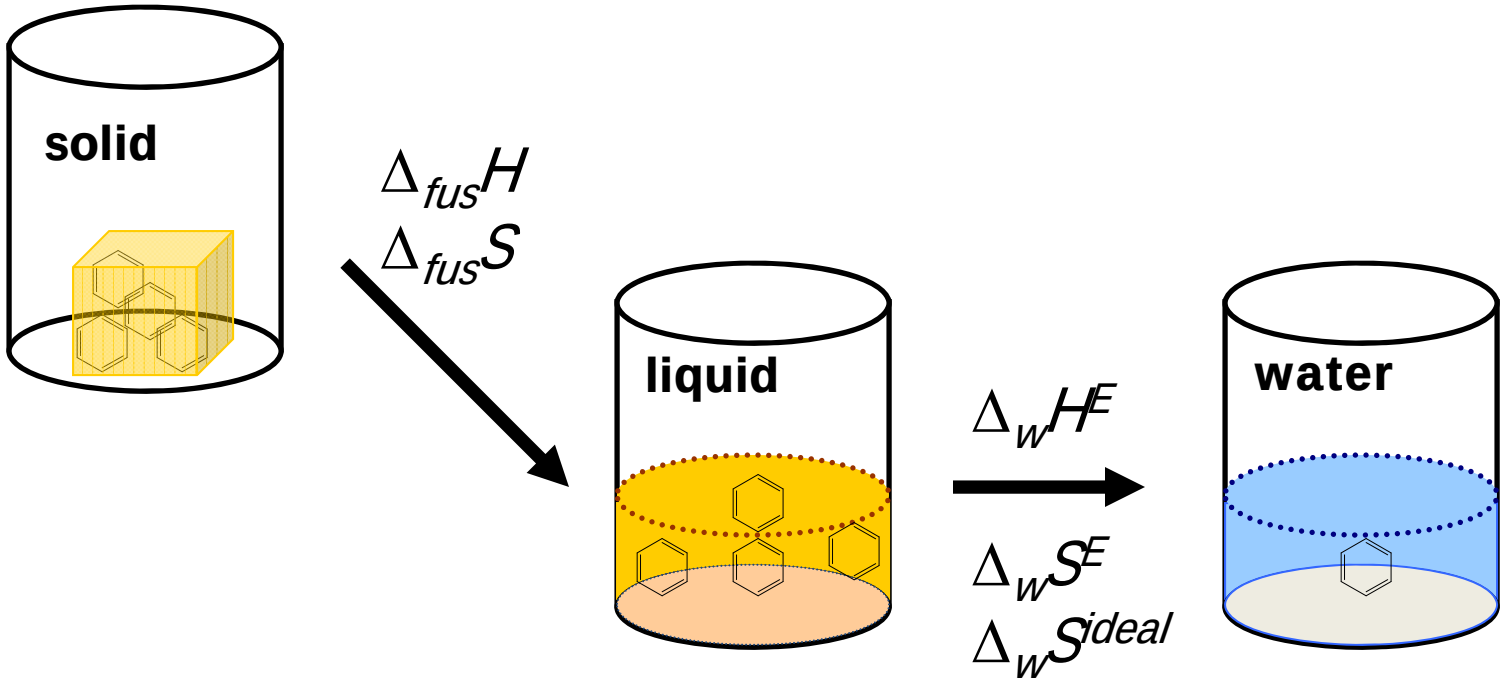
Organic Liquid	x_o	Reference
Pentane	0.99952	
Hexane	0.99946	
Heptane	0.99916	Gerrard, 1980
Octane	0.99911	
Benzene	0.9977	
Chlorobenzene	0.9975	
1,2,-Dichlorobenzene	0.9973	
1,2,4-Trichlorobenzene	0.9980	
Trichloroethylene	0.9977	Horvath, 1982
Tetrachloroethylene	0.99913	
Methylene chloride	0.9914	
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	

TABLE 5.2 Aqueous Solution Activity Coefficients γ_w^∞ of Some Sparingly Soluble Organic Compounds in Infinitely Dilute Solutions[a]

Compound	γ_w^∞
Benzene	2.4×10^3
Toluene	1.2×10^4
Naphthalene	1.4×10^5
Phenanthrene	7.4×10^6
Benzo(a)pyrene	2.8×10^9
Methylene chloride	4.2×10^2
Chloroform	8.6×10^2
Carbon tetrachloride	1.0×10^4
1,1,1-Trichloroethane	2.4×10^3
Chlorobenzene	1.9×10^4
1,3-Dichlorobenzene	1.7×10^5
1,2,3,5-Tetrachlorobenzene	1.4×10^7
Pentachlorobenzene	1.2×10^8
Hexachlorobenzene	9.8×10^8
2,4′-Dichlorobiphenyl	5.8×10^7
2,2′,5,5′-Tetrachlorobiphenyl	4.2×10^9
2,2′,4,4′,5,5′-Hexachlorobiphenyl	2.9×10^{11}
Methyl ethyl ketone	3.2×10^1
Diethyl ether	1.6×10^2
Ethyl acetate	1.5×10^2
Octanol	3.7×10^3

[a]After Banerjee, 1985.

Aqueous Solubility



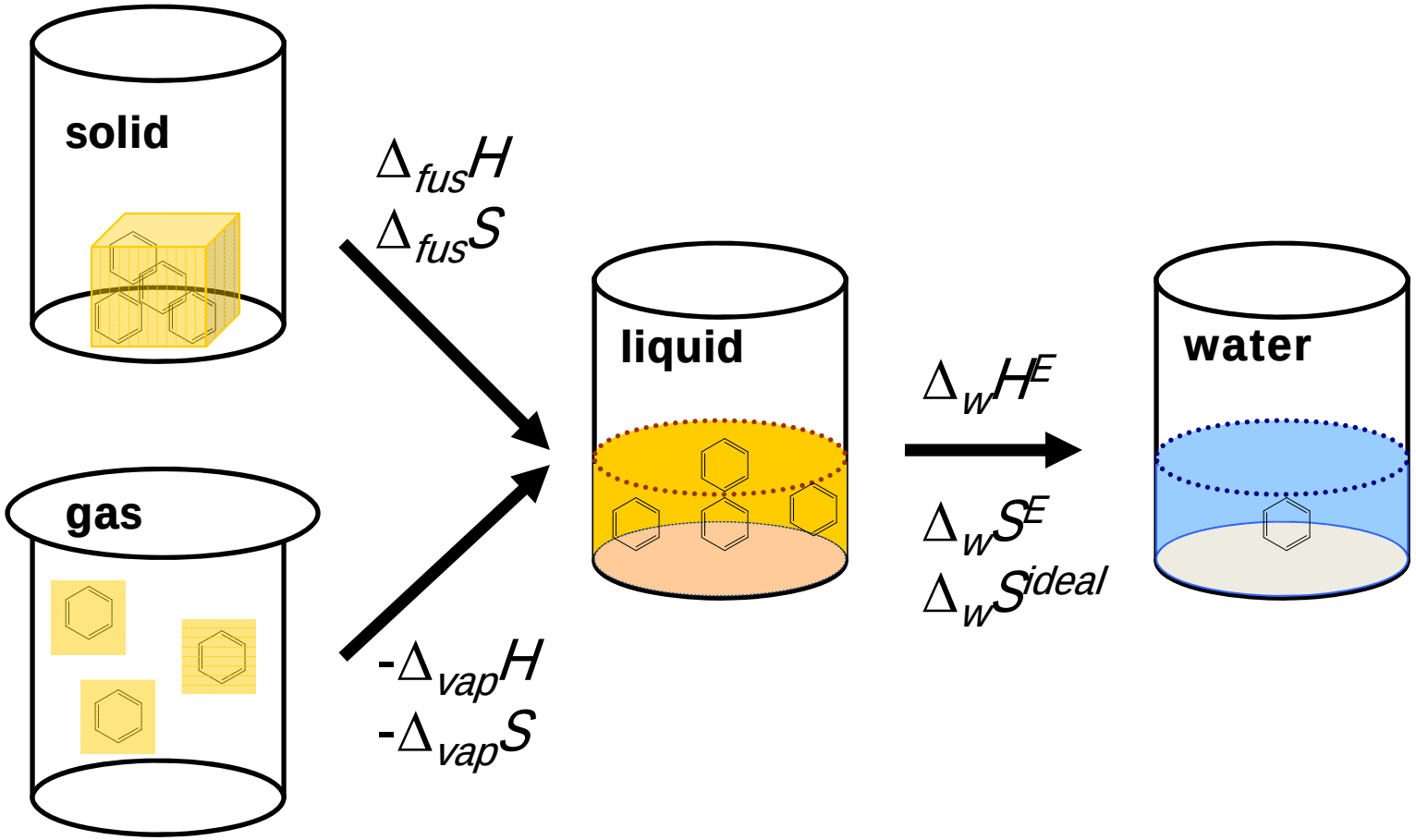
Aqueous Solubility

- Solubility of an organic solid
  - pure solid $\Rightarrow$ pure liquid (melting)
  - pure liquid $\Rightarrow$ water (dissolution)

$$\Delta_w G = RT \ln x_w + RT \ln \gamma_w - RT \ln \frac{p_s^*}{p_L^*}$$

$\Delta_{fus}G$: melting costs
- need more heat, $\Delta_{fus}H$
- further increase in entropy, $\Delta_{fus}S$

Aqueous Solubility



Aqueous Solubility

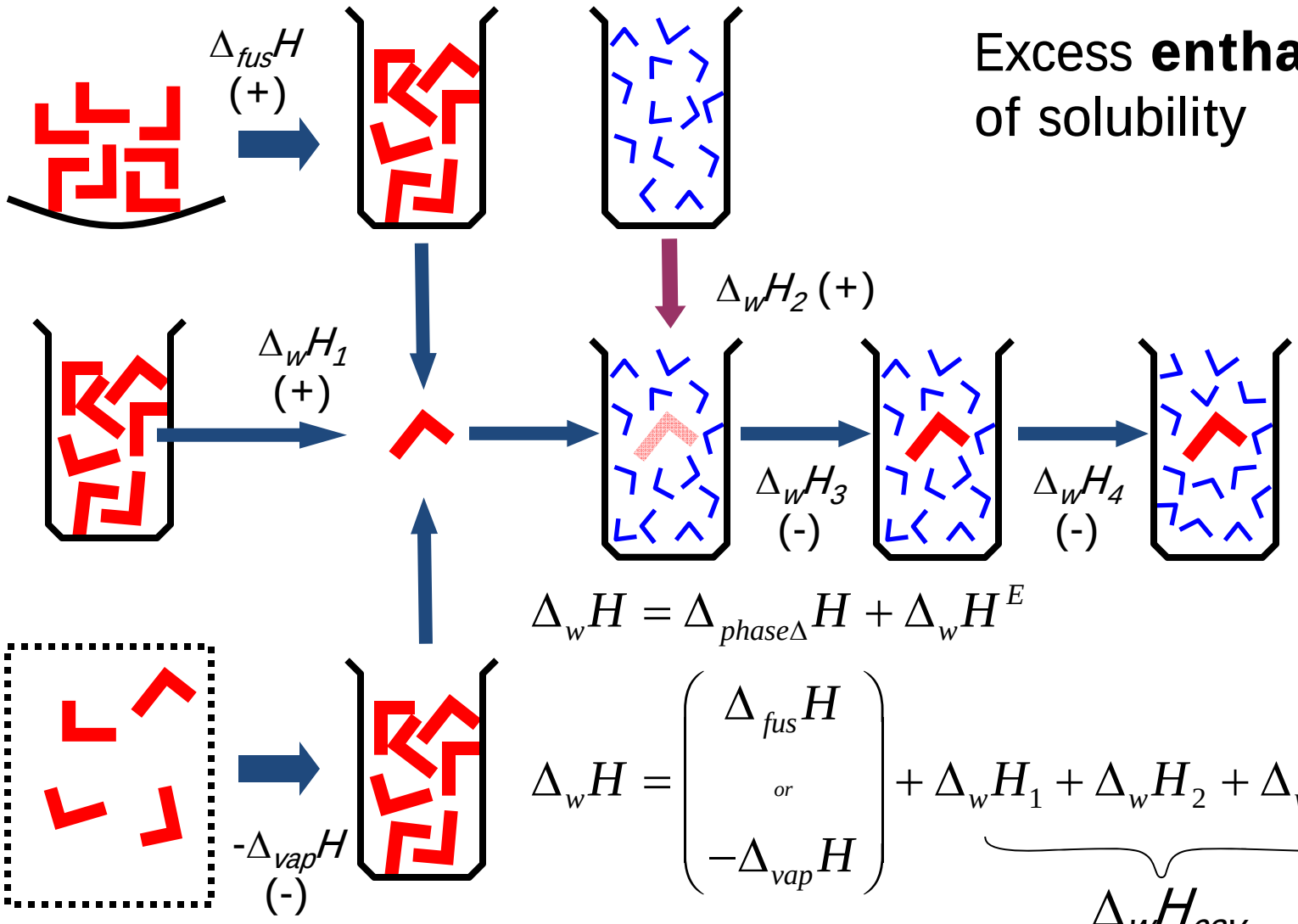
- Solubility of an organic gas
  - pure gas $\Rightarrow$ pure liquid (condensation)
  - pure liquid $\Rightarrow$ water (dissolution)

  - p = 1 bar

$$\Delta_w G = RT \ln x_w + RT \ln \gamma_w - RT \ln \frac{p}{p_L^*}$$

$\Delta_{cond}G$: condensation "income"
- removing heat, $\Delta_{cond}H$
- decreasing entropy, $\Delta_{cond}S$

Aqueous Solubility



Excess **enthalpy** of solubility

$$\Delta_w H = \Delta_{phase\Delta} H + \Delta_w H^E$$

$$\Delta_w H = \begin{pmatrix} \Delta_{fus} H \\ or \\ -\Delta_{vap} H \end{pmatrix} + \underbrace{\Delta_w H_1 + \Delta_w H_2 + \Delta_w H_3}_{\Delta_w H_{cav}} + \Delta_w H_4 \qquad \Delta_w H_{ice}$$

Excess **enthalpy** of solubility

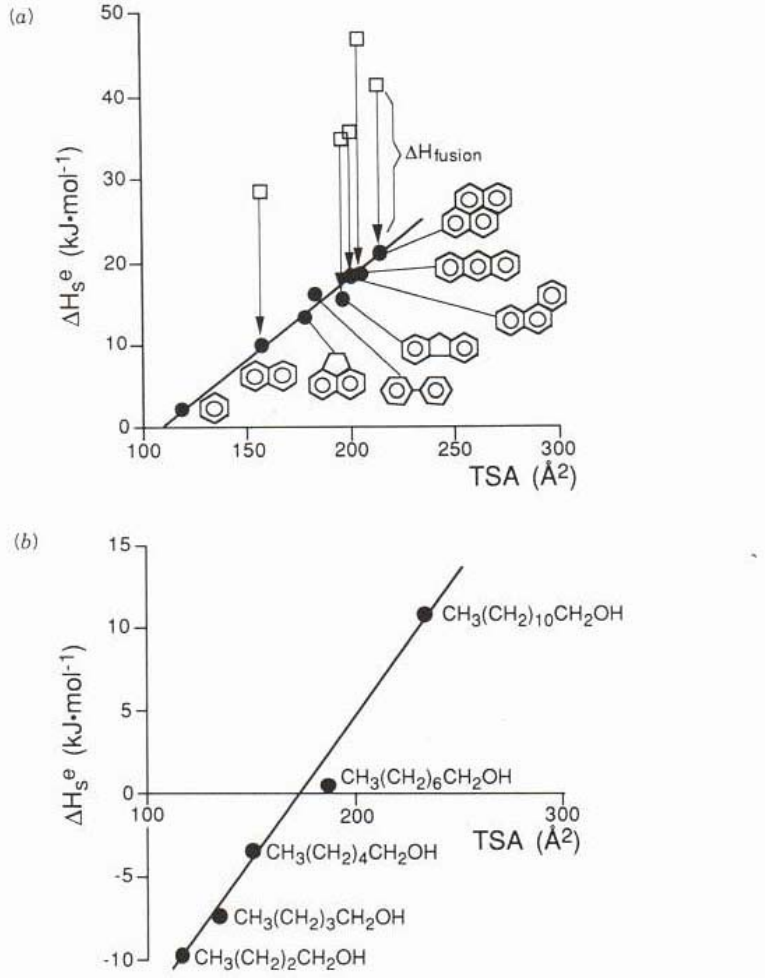
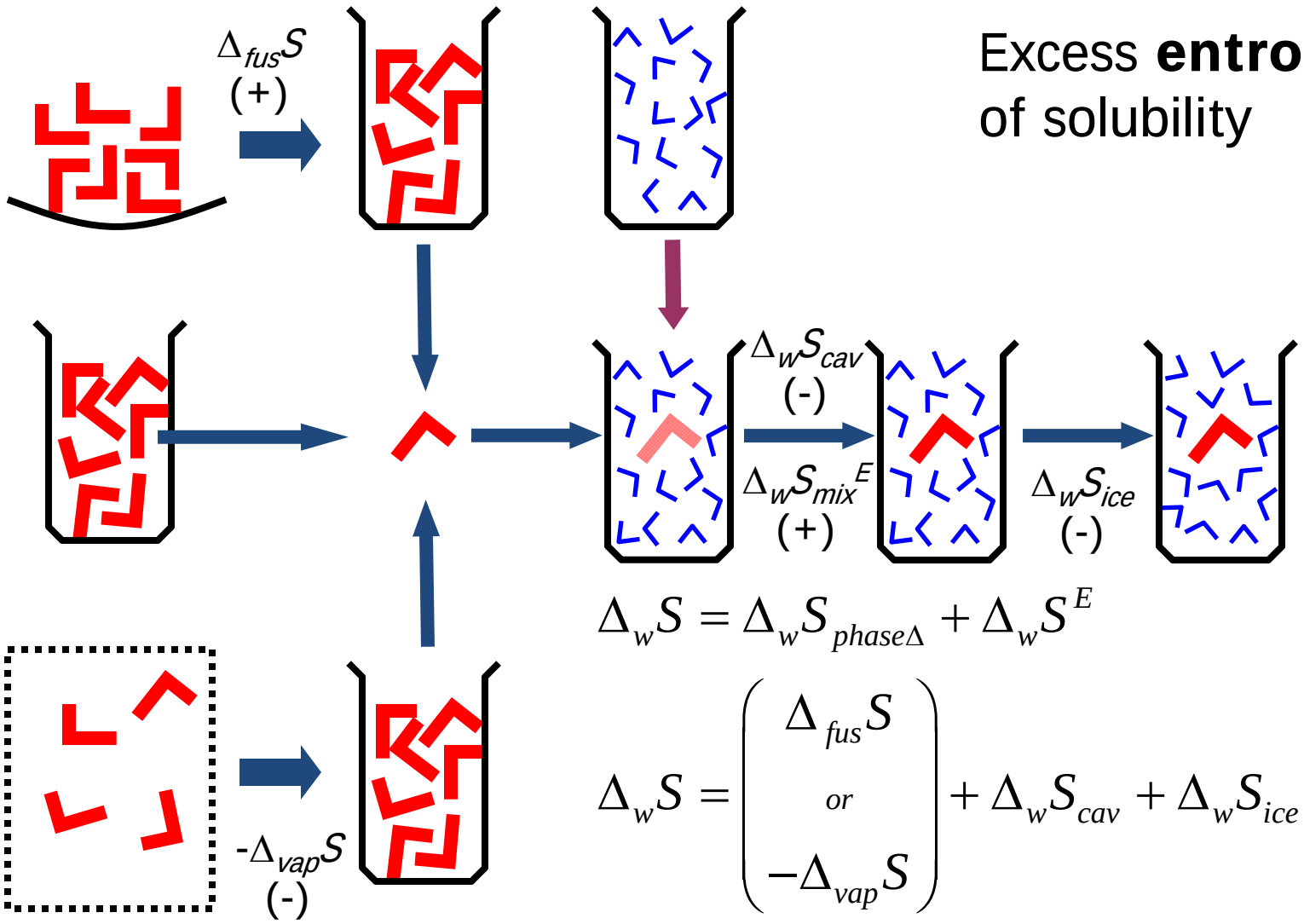


Figure 5.3 Enthalpies of solution of *liquid* organic compounds in water at 25°C versus their total surface areas (TSA): (*a*) a series of nonpolar compounds, (*b*) a series of compounds exhibiting a polar functional group.

NON-POLAR

POLAR

Aqueous Solubility



Excess **entropy** of solubility

$$\Delta_w S = \Delta_w S_{phase\Delta} + \Delta_w S^E$$

$$\Delta_w S = \begin{pmatrix} \Delta_{fus} S \\ or \\ -\Delta_{vap} S \end{pmatrix} + \Delta_w S_{cav} + \Delta_w S_{ice} + \Delta_w S^E_{mix}$$

Excess **entropy** of solubility

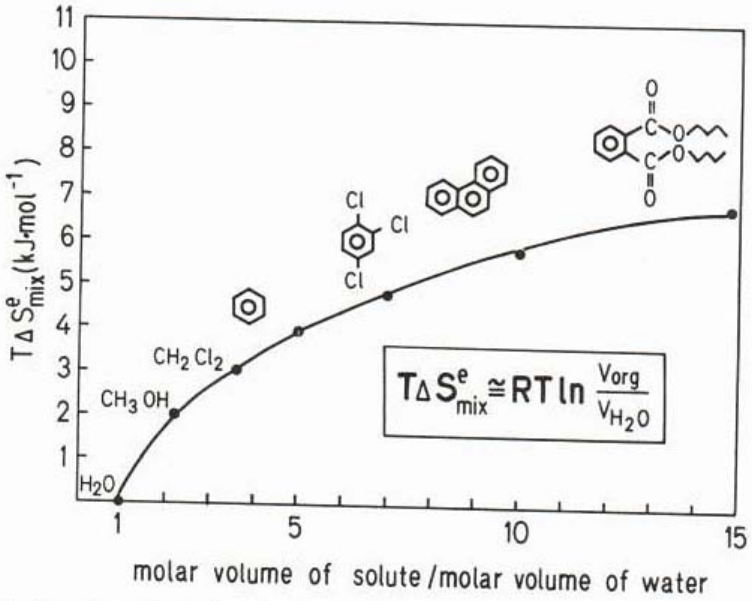


Figure 5.4 Contribution of molecular size to the entropy of dissolution of an organic compound in water.

TABLE 5.3 Entropies of Solution for Liquids (Real or Subcooled) at 25°C[a]

Compound	ΔS^e_s (J·mol^{-1}·K^{-1})
Aromatic Compounds	
Benzene	−58
Naphthalene (L)	−59
Acenaphthene (L)	−52
Fluorene (L)	−62
Phenanthrene (L)	−61
Anthracene (L)	−60
Pyrene (L)	−48
Mean =	−57 ± 5
n-Alcohols	
Methanol	−29
Ethanol	−44
Propanol	−51
Butanol	−65
Pentanol	−71
Hexanol	−68
Octanol	−76
Dodecanol	−92

[a] Entropies estimated from data shown in Table 5-4.

Aqueous Solubility

- At equilibrium ($\Delta_w G = 0$)

$$\Delta_w G = RT \ln x_w + RT \ln \gamma_w = 0$$

$$RT \ln x_w = -RT \ln \gamma_w$$

$$\ln x_w = -\ln \gamma_w$$

$$\ln x_w = \ln \frac{1}{\gamma_w}$$

$$x_w = \frac{1}{\gamma_w}$$

Aqueous Solubility

- At equilibrium ($\Delta_w G = 0$)

$$\Delta_w G = RT \ln x_w + RT \ln \gamma_w$$

liquid	$x_w^{sat} = \frac{1}{\gamma_w^{sat}}$
solid	$x_w^{sat} = \frac{1}{\gamma_w^{sat}} \frac{p_s^*}{p_L^*}$
gas	$x_w^{sat} = \frac{1}{\gamma_w^{sat}} \frac{1\text{bar}}{p_L^*}$

Aqueous Solubility

- At equilibrium ($\Delta_w G = 0$)

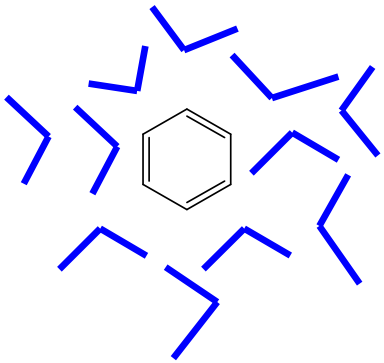
liquid	$C_w^{sat} = \frac{1}{\overline{V}_w \gamma_w^{sat}}$
solid	$C_w^{sat} = \frac{1}{\overline{V}_w \gamma_w^{sat}} \frac{p_s^*}{p_L^*}$
gas	$C_w^{sat} = \frac{1}{\overline{V}_w \gamma_w^{sat}} \frac{1\text{bar}}{p_L^*}$

$$C_w^{sat} = \frac{x_w^{sat}}{\overline{V}_w}$$

Aqueous Solubility

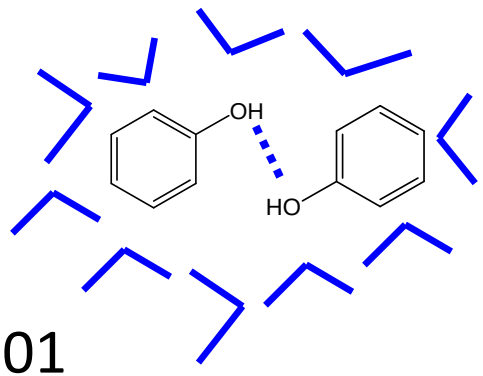
- Activity coefficient
  - for low solubility compounds:

$$\gamma_w^{sat} \approx \gamma_w^{\infty} \quad (\gamma_w^{\infty} \text{ is } \gamma_w)$$



  - for high solubility compounds

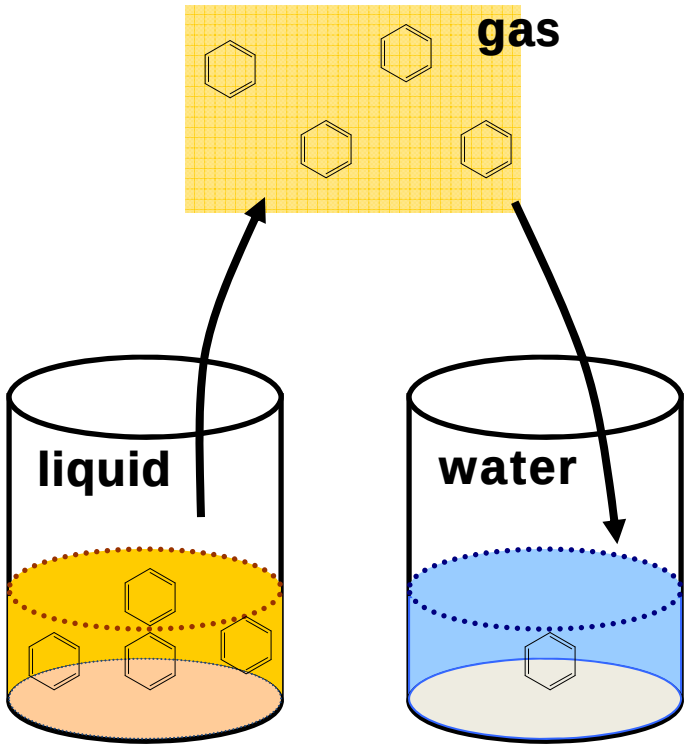
$$\gamma_w^{sat} < \gamma_w^{\infty}$$



  - solubility defined two ways:
    - "low solubility" as $\gamma_w > 100$
    - "high solubility" as volume fraction >0.01

Aqueous Solubility

- Relate γ_w to other properties
  - from pure liquid to vapor
    - described by p_L^*
  - from vapor to water
    - size of cavity
      - molar volume of solute
    - solute-water interactions
      - van der Waals
      - hydrogen bonding



Aqueous Solubility

- Relate γ_w to other properties (Eqn. 5-22)

vdW forces

size

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

vapor pressure of solute as a liquid (bar)

molar volume of solute as a liquid

refractive index of solute

dipolarity/ polarizability descriptor (Table 5.5)

H-bond descriptor for H-donor (Table 4.3)

H-bond descriptor for H-acceptor (Table 4.3)

$$\Delta G_s^e = \Delta H_s^e - T\Delta S_e^e = (\Delta H_{cavity} + \Delta H_{ice}) - T(\Delta S_{ice} + \Delta S_{mixing}^e) = RT \ln \gamma_w$$

TABLE 5.4 Comparisons of Enthalpic and Entropic Contributions to Excess Free Energies of Solutions at 25°C

Compound	ΔG_s^e $(= -RT \ln x(l, L))^a$ $(kJ \cdot mol^{-1})$	ΔH_s^e $(= \Delta H_s - \Delta H_m)^b$ $(kJ \cdot mol^{-1})$	$-T\Delta S_s^e$ $(= \Delta G_s^e - \Delta H_s^e)$ $(kJ \cdot mol^{-1})$
Benzene	19.3	2.1	17.2
Naphthalene (L)	27.6	9.9	17.7
Acenaphthene (L)	28.8	13.4	15.4
Fluorene (L)	34.0	15.5	18.5
Phenanthrene (L)	36.3	18.1	18.2
Anthracene (L)	36.4	18.4	18.0
Pyrene (L)	40.6	26.4	14.2
Methanol	1.3	−7.4	8.7
Ethanol	2.4	−10.7	13.1
Propanol	6.2	−8.9	15.1
Butanol	9.6	−9.7	19.3
Pentanol	13.7	−7.4	21.1
Hexanol	16.8	−3.5	20.3
Octanol	23.1	0.5	22.6
Dodecanol	38.0	10.7	27.3

[a] Liquid solubilities are given in the Appendix.

[b] Free energies and enthalpies of solution of aromatic hydrocarbons from May et al. (1983). Enthalpies of fusion of aromatic hydrocarbons from Wauchope and Getzen (1972). Free energies of solution of alcohols from data of Butler et al. (1935) and enthalpies of solution of alcohols from data of Stephenson et al. (1984). Enthalpies of fusion of benzene and alcohols are not subtracted since these are liquids. The products, [illegible] estimated by difference.