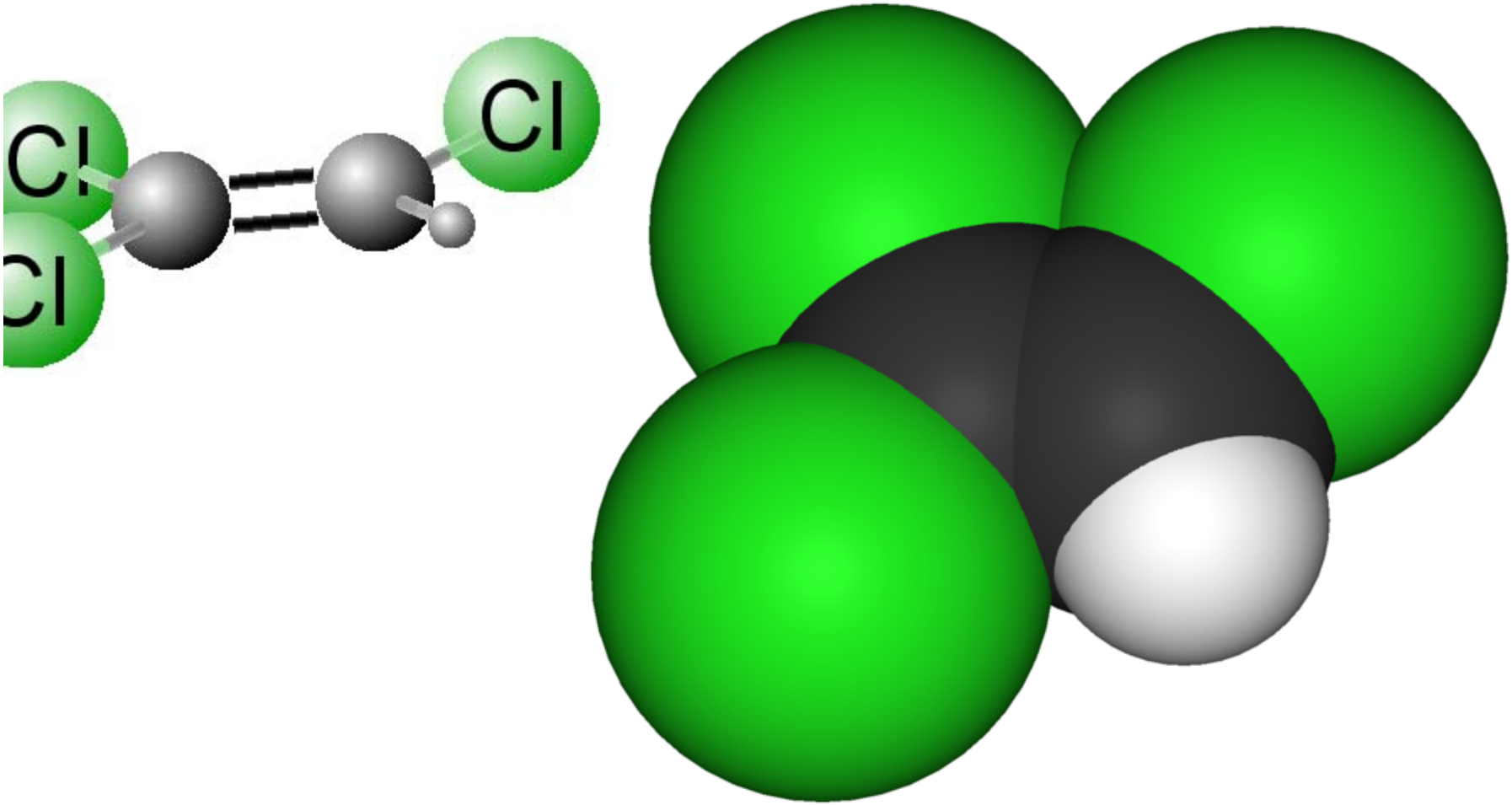
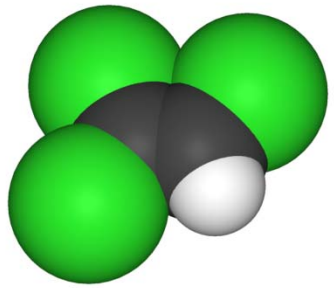
Interesting molecule of the day

- Trichloroethene (TCE)

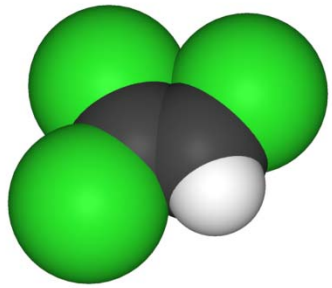


Interesting molecule of the day



- Trichloroethene (1,1,2-trichoroethene)
  - industrial solvent – degreaser
    - replacement for chloroform
    - anesthetic (1930s-1960s) until toxicity detected
  - toxicity
    - depression of central nervous system
    - cancer (kidney, liver)
    - congenital heart defects, fertility
  - major groundwater contaminant
    - 852 Superfund sites
    - 34% of drinking water supplies (MCL 5 µg L^{-1})
    - vapor intrusion and indoor air contamination

Interesting molecule of the day



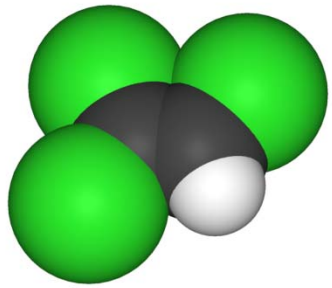
- Trichloroethene, IBM, and Endicott, NY
  (Business Week, Jan 10, 2008)
  - IBM manufacturing plant
    - 12,500 employees in 1984,
      down to 1,200 today
    - TCE spills
      - groundwater cleanup since 1979
      - ventilation for 458 homes

  - lawsuits
    - 94 residents, businesses;
      900 more to follow
    - exposure by vapors; cancer, birth defects
  - "TCE is the new PCB"
    - Ellen Relkin, attorney, Weitz & Luxenberg, NY, NY

Interesting molecule of the day

TCE and Military

TCE and the Air force

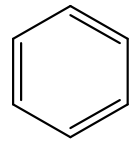


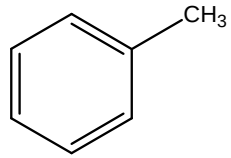
Aqueous Solubility

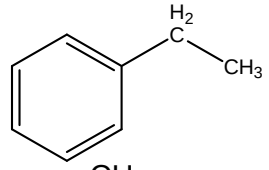
- What affects solubility? (or activity coefficient)
- Structure
- Temperature
- Ionic strength
- Cosolvents/Cosolutes

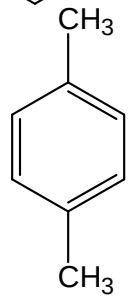
Aqueous Solubility

- Rank the following compounds by aqueous solubility from highest to lowest.

benzene 

toluene 

ethylbenzene 

p-xylene 

A. ethylbenzene > *p*-xylene > toluene > benzene

B. benzene > toluene > ethylbenzene > *p*-xylene

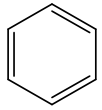
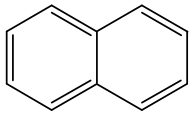
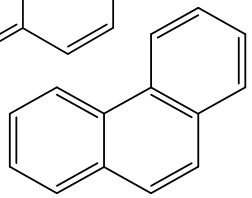
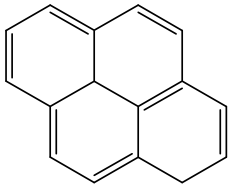
C. benzene > toluene > *p*-xylene ≈ ethylbenzene

C_w^{sat}	0.022 M	0.0060 M	0.0016 M	0.0017 M

Aqueous Solubility

- Which of the following compounds is least soluble in water?

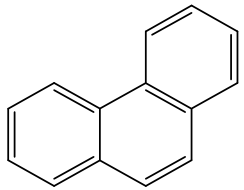
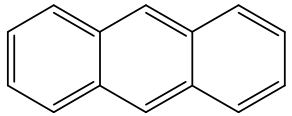
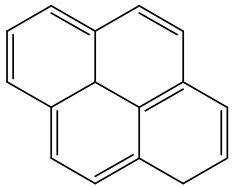
Dalton: one-twelfth the weight of an atom of ^{12}C

	compound		molecular weight (Da)
A	benzene		78.1
B	naphthalene		128.2
C	phenanthrene		178.2
D	pyrene		202.3

Aqueous Solubility

$$\ln C_{iw}^{sat}(L) = -c \cdot (size_i) + d$$

- Which of the following compounds is least soluble in water?

	compound		molecular weight (Da)
A	phenanthrene		178.2
B	anthracene		178.2
C	pyrene		202.3

Aqueous Solubility

- What affects solubility?
  (or activity coefficient)
- Structure
- Temperature
- Ionic strength
- Cosolvents/Cosolutes

$$\log C_w^{sat} = -\frac{\Delta H_s^e}{2.303RT} + \text{constant}$$

Aqueous Solubility

- Temperature dependence
  - liquid
    - small $\Delta_w H^E$
    - small temperature effect

$$\ln C_w^{sat}(L) = -\frac{\Delta_w H^E}{R}\frac{1}{T} + c$$

  - solid
    - small $\Delta_w H^E$, large $\Delta_{fus} H$
    - large temperature effect

$$\ln C_w^{sat}(s) = -\frac{\left(\Delta_{fus} H + \Delta_w H^E\right)}{R}\frac{1}{T} + c$$

  - gas
    - small $\Delta_w H^E$, large $\Delta_{cond} H$
    - large temperature effect

$$\ln C_w^{p=1bar}(g) = -\frac{\left(-\Delta_{vap} H + \Delta_w H^E\right)}{R}\frac{1}{T} + c$$

Aqueous Solubility

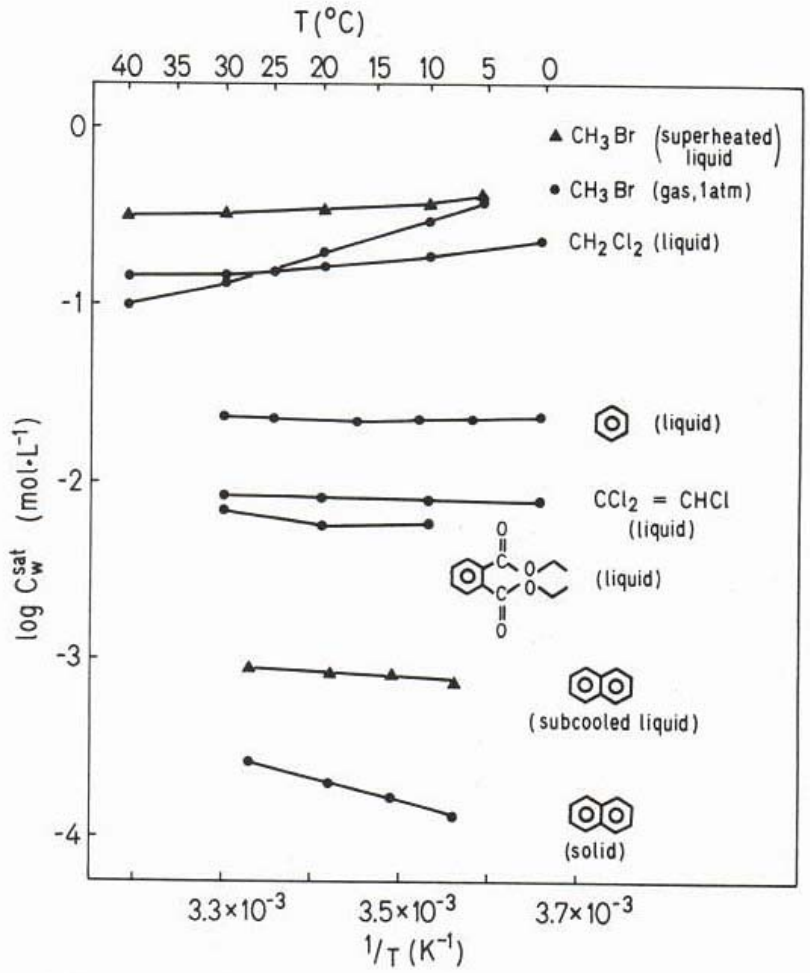


Figure 5.6 Solubility in water as a function of temperature for various compounds.

Range 0 – 35°C

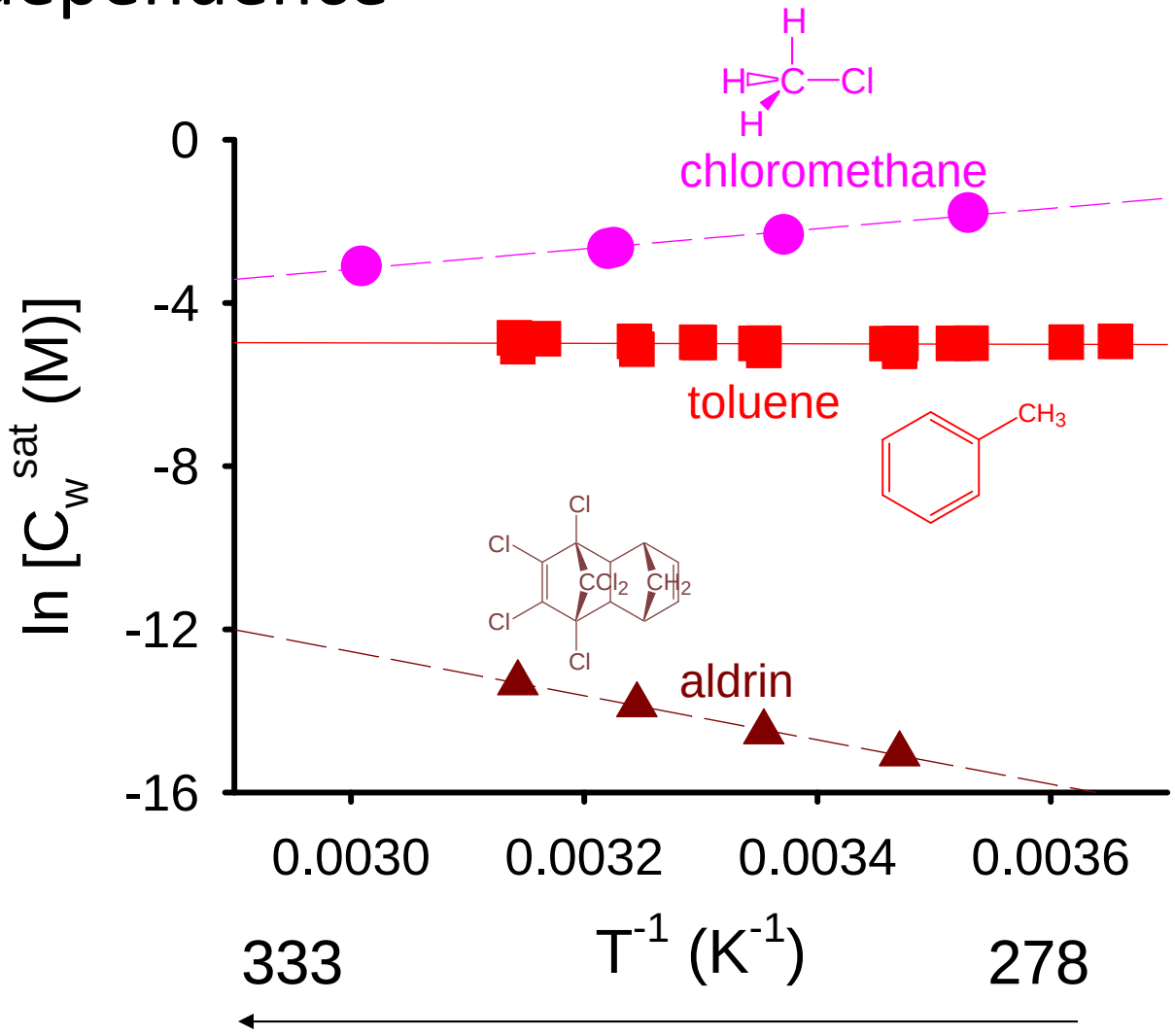
92 SOLUBILITY AND ACTIVITY COEFFICIENT IN WATER

TABLE 5.5 Effect of Temperature on the Solubility of Organic Liquids and Solids

Compound (State)	T_1 (°C)	$-\log C_w^{sat}$ (mol·L^{-1})	T_2 (°C)	$-\log C_w^{sat}$ (mol·L^{-1})	$C_w^{sat}(T_2)/C_w^{sat}(T_1)$
1-Pentanol (l)	≈0	0.42	30.6	0.64	1.7
1-Heptanol (l)	≈0	1.69	30.6	1.88	1.5
Tetrachloroethylene (l)	≈0	3.04	30.0	3.04	1.0
1,1,1-Trichloroethane (l)	≈0	1.84	30.0	1.96	1.3
1,2-Dichlorobenzene (l)	≈0	3.51	30.0	3.16	2.2
Phenanthrene (s)	4.0	5.69	29.9	5.16	3.4
Phenanthrene (L)	4.0	4.67	29.9	4.48	1.5
Anthracene (s)	5.2	7.15	29.3	6.49	4.6
Anthracene (L)	5.2	4.88	29.3	4.64	1.7

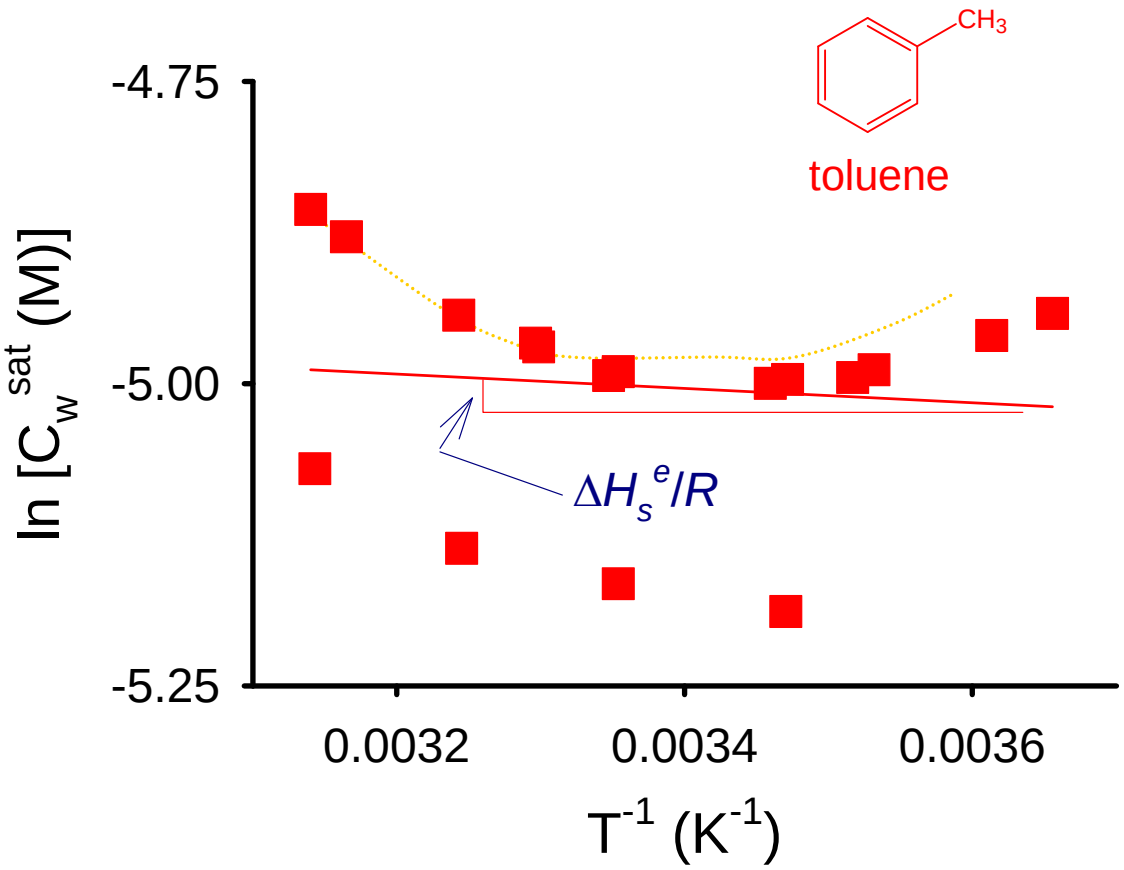
Aqueous Solubility

- Temperature dependence
  - gas
    - ln C_w^{sat} $\propto$ 1/T
  - liquid
    - ln C_w^{sat} ?
  - solid
    - ln C_w^{sat} $\propto$ T



Aqueous Solubility

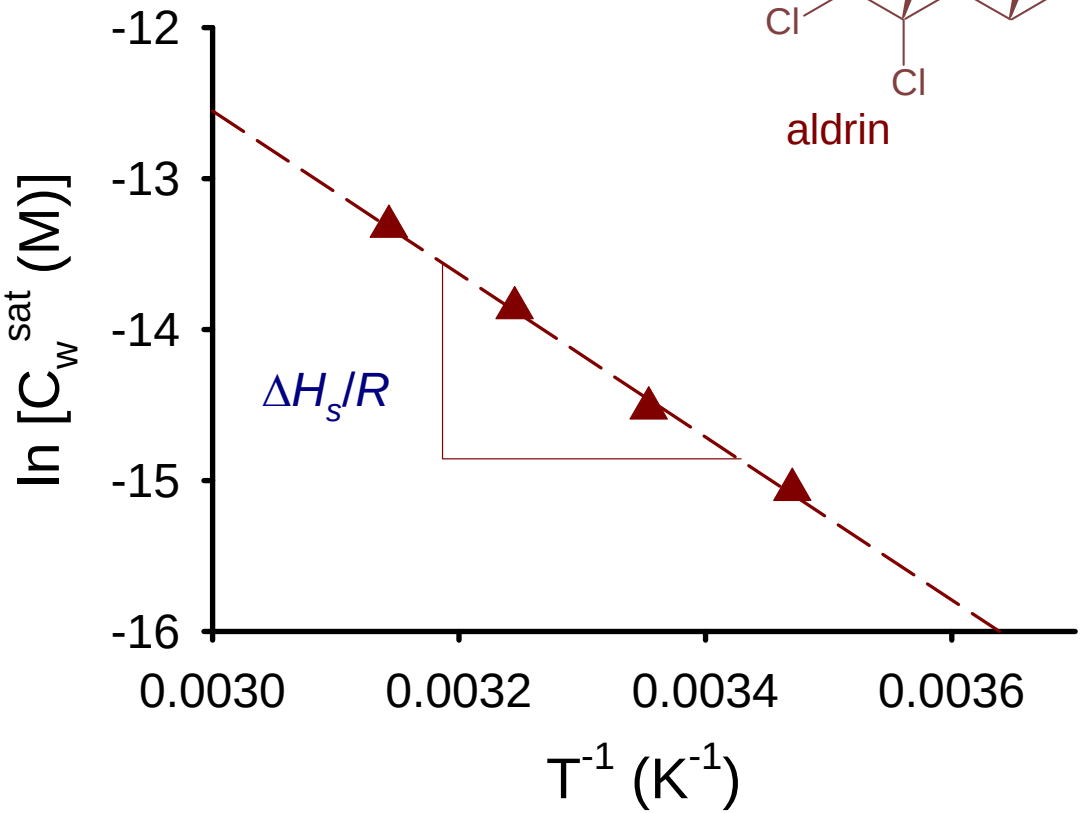
- Liquid
  - slope is $-\Delta_w H^E/R$ over T range of interest
  - slope is not constant
  - $\Delta_w H^E$ is not constant



Aqueous Solubility

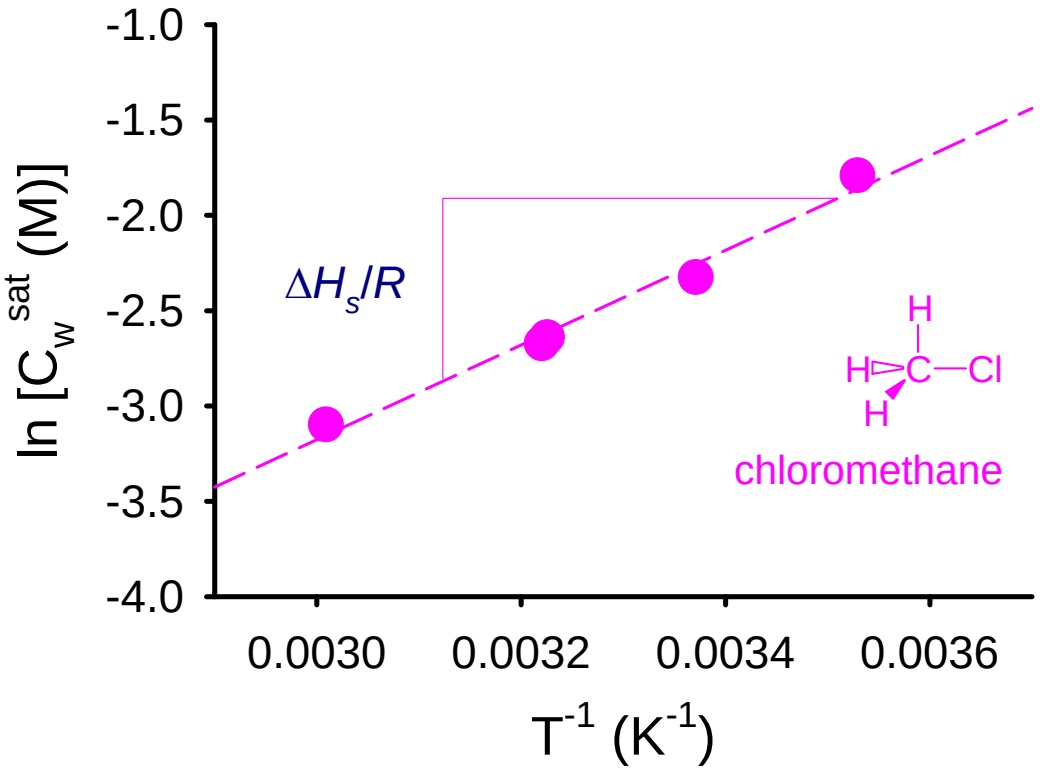
- Solid
  - slope is $-(\Delta_{fus}H + \Delta_w H^E)/R$
  - Usually, $\Delta_{fus}H > \Delta_w H^E$

aldrin



Aqueous Solubility

- Gas
  - slope is
    $-(-\Delta_{vap}H + \Delta_{w}H^{E})/R$
  - Usually,
    $-\Delta_{vap}H > \Delta_{w}H^{E}$



Aqueous Solubility

- Salt in water (Na^+, K^+, Ca^{+2}, Mg^{+2}, Cl^-, $SO_4^=$,HCO_3^-)
  - "electrostriction"
  - water forms hydration shells around ions
  - less water available for compound to dissolve into
- "Salting out"
  - decreases solubility of nonpolar organic compounds

Aqueous Solubility

$$\log\left[\frac{C_w^{sat}}{C_{w,salt}^{sat}}\right] = K^s[salt]$$

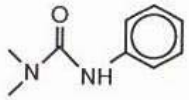
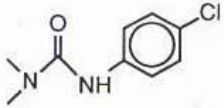
- Setschenow equation

$$C_{w,salt}^{sat} = 10^{-K^S[salt]_{tot}} C_w^{sat} \quad \text{(Eqn. 5-27)}$$

- Setschenow constant K^S
  - compound-specific (increases with decreasing C_w^{sat})
  - salt-specific (increases with increasing ion hydration)
- total molar salt concentration $[salt]_t$ $K^s = \sum_i K_i^s \bullet x_i$
  - single salt or mixture of salts (e.g., seawater)

Aqueous Solubility

TABLE 5.6 Salting Constants for Some Aromatic Compounds in Seawater (sw), Artificial Seawater (art sw), and Sodium Chloride Solutions (NaCl) at 25°C

Compound	TSA (Å²)	Salting Constant K^s (L·mol⁻¹)			Reference[a]		
		sw	art sw	NaCl	sw	art sw	NaCl
Benzene	110			0.18, 0.19			a, b
Naphthalene	156	0.25, 0.28	0.30	0.21, 0.19, 0.22	d, c	e	a, c, d
Phenanthrene	198	0.25, 0.33	0.39	0.27, 0.29	f, c	e	a, c
Anthracene	202	0.26, 0.35		0.24, 0.25	f, c		a, c
Pyrene	213	0.31, 0.32		0.29, 0.29	c, g		a, c
Chrysene	241			0.34			a
Biphenyl		0.41	0.41	0.26	c	e	c
2,4′-Dichlorobiphenyl		0.3			i		
2,4,4′-Trichlorobiphenyl		0.4			i		
2,3′,4′,5-Tetrachlorobiphenyl		0.2			i		
2,2′,3,4,5′-Pentachlorobiphenyl		0.3			i		
2,2′,3,4,4′,5-Hexachlorobiphenyl		0.3			i		
Toluene (methylbenzene)		0.17	0.28			h	g
Phenol (hydroxybenzene)		0.13		0.12	c		c
4-Aminotoluene		0.19		0.17	c		c
4-Nitrotoluene		0.11		0.14	c		c
Fenuron				0.23			j
Monuron				0.24			j

[a] May (1980).
[b] McDevit and Long (1952).
[c] Hashimoto et al. (1984).
[d] Gordon and Thorne (1967b).
[e] Eganhouse and Calder (1976).
[f] Whitehouse (1984).
[g] Rossi and Thomas (1981).
[h] Sutton and Calder (1975).
[i] Brownawell (1986).
[j] van Bladel and Moreale (1974).

Aqueous Solubility

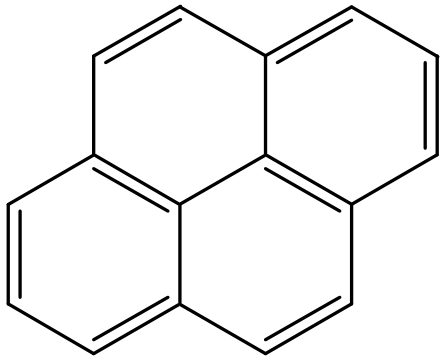
TABLE 5.7 Salting Constants for Benzene and Naphthalene at 25°C for Some Important Salts

Salt	Mole fraction in seawater[a] x_i	Salting Constant K^s (benzene)[b] ($L \cdot mol^{-1}$)	Salting Constant K^s (naphthalene) ($L \cdot mol^{-1}$)
NaCl	0.799	0.19	0.22
$MgCl_2$	0.104		0.30
Na_2SO_4	0.055	0.55	0.70
$CaCl_2$	0.020		0.32
KCl	0.018	0.17	0.19
$NaHCO_3$	0.005		0.32
KBr		0.12	0.13
CsBr			0.01

[a] Gordon and Thorne (1967a, b).
[b] McDevit and Long (1952).

Aqueous Solubility

- Example: pyrene "salting out" of seawater
  - C_w^{sat} (25°C) = $10^{-6.16}$ M
  - K^S = 0.30 (Table 5.7 for seawater)
  - $[salt]_T \approx 0.5$ M
    - {[cations (M)] + [anions (M)]}/2

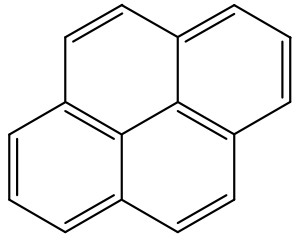


Aqueous Solubility

- Example: pyrene

$$C_{w,salt}^{sat} = 10^{-K^S[salt]_t} C_w^{sat} = 0.71 C_w^{sat}$$

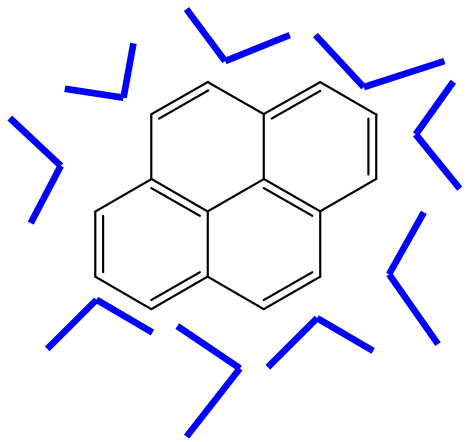
$$C_{w,salt}^{sat} = 0.71\left(10^{-6.16}\right) = 10^{-6.31}\ \mathrm{M}$$



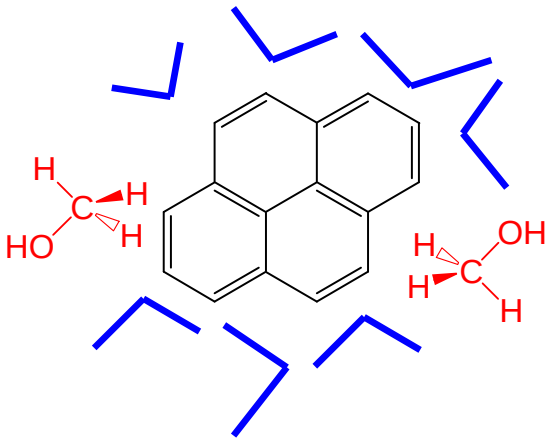
  - seawater reduces solubility by about 29%

Aqueous Solubility

- Co-solvents in water
  - high solubility organic compounds
  - replace water in cavity around nonpolar organic compound
- Increase solubility
  - more favorable interactions with nonpolar organic compound

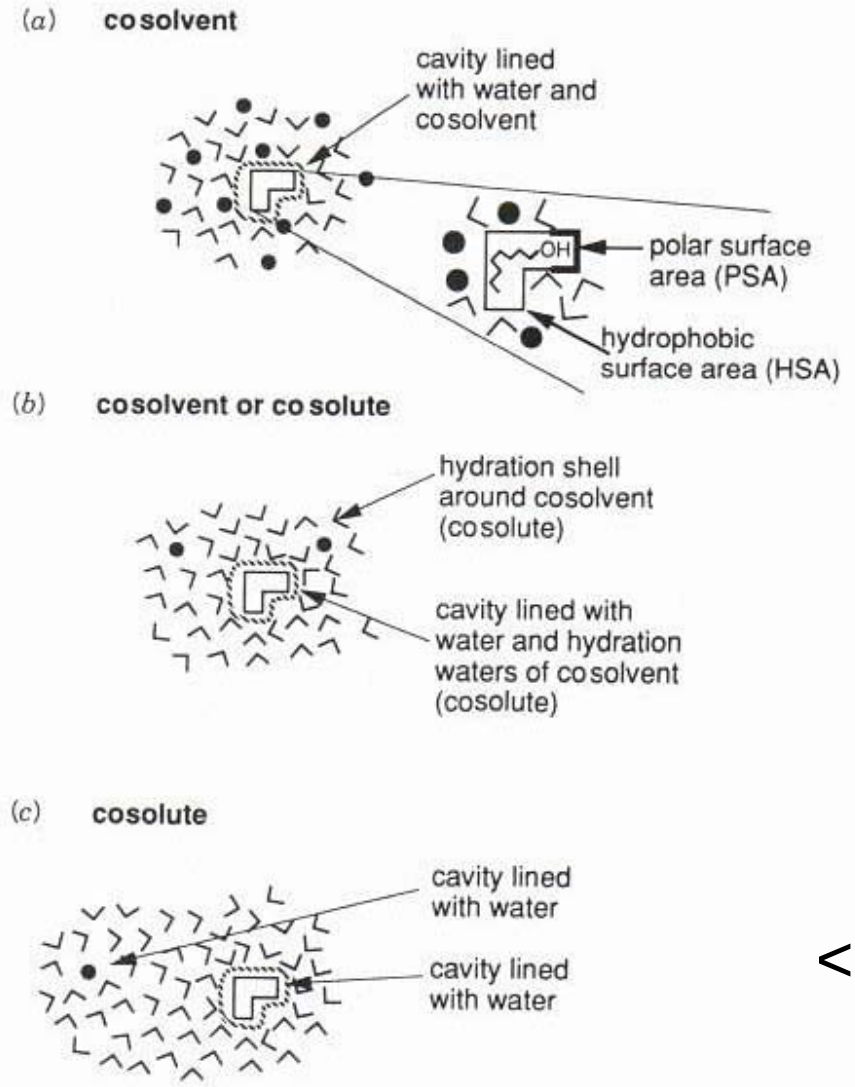


pyrene in pure water



pyrene in 20% methanol solution

Aqueous Solubility



>10% V/V

saturation

<10^{-3} volume fraction

Figure 5.8 Illustrations of how other dissolved organic substances (●) affect the water molecules surrounding an organic compound of interest (⌐).

Aqueous Solubility

- Estimate solubility in co-solvent mixture

$$\gamma_{il}(f_v) = 10^{-\sigma_i^c f_v}\,\gamma_{iw} \qquad \text{(Eqn. 5-33)}$$

  - γ_{il} activity coefficient in co-solvent/water mix
  - γ_{iw} activity coefficient in pure water
  - σ_i^c "co-solvency power" (depends on f_v)
  - fractional volume of co-solvent in water f_v

Aqueous Solubility

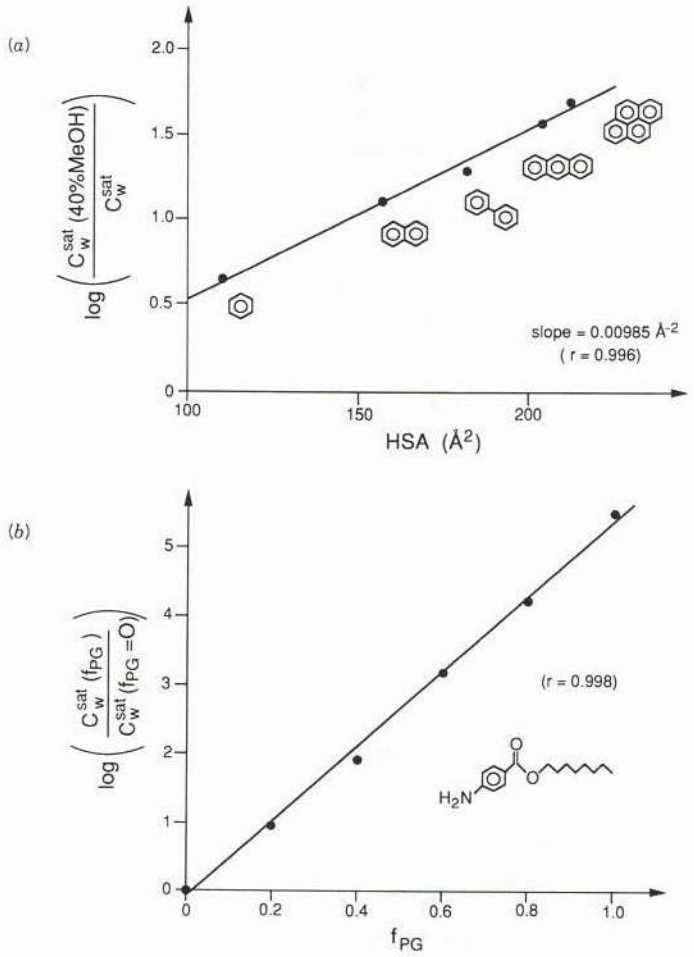


Figure 5.9 Illustration of cosolvent-enhanced solubility as a function of (*a*) the hydrophobic surface area (HSA in Å^2) of a set of aromatic solutes (data from Morris et al., 1988) and (*b*) the fraction of propylene glycol in aqueous solutions of *n*-octyl-*p*-amino-benzoate (data from Yalkowsky et al., 1976).

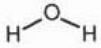
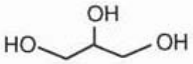
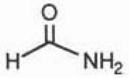
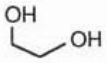
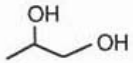
HSA hydrophobic surface area

Pyrene >>> Benzene (log)

Fraction of co-solvent

Aqueous Solubility

TABLE 5.8 Estimated Solubility Enhancement of Pyrene (HSA = 212 Å^2) for Solutions Containing 10% Cosolvent at 20°C[a]

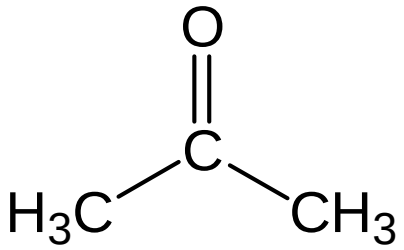
Cosolvent	Structure	Liquid:Air Surface Tensions at 20°C[d] (erg/cm^2)	$\sigma_{t:c}$ (erg/cm^2)	$\sigma_{t:w} - \sigma_{t:c}$ (erg/cm^2)	$\frac{C_{mix}^{sat}}{C_w^{sat}}$
Water		73	52	0	1
Glycerin		63	35	17	1.6[b]
Formamide		58	31	21	1.7
Ethylene glycol		48	19	33	2.3[b], 1.9[c]
Propylene glycol		—	13	39	2.8[b], 2.5[c]
Isopropanol		22	<10[e]	~ 52	3.9[b], 3.3[c]
Methanol	CH_3OH	23	<10[e]	~ 52	3.9[b], 2.8[c]
Ethanol		23	<10[e]	~ 52	3.9[b], 3.3[c]
Acetonitrile	$CH_3-C\equiv N$	29	<10[e]	~ 52	3.9[b], 3.6[c]
Acetone		24	<10[e]	~ 52	3.9[b], 3.6[c]

[a] Also shown are liquid:air surface tensions, liquid:tetradecane surface tensions ($\sigma_{t:c}$), and an estimated value of the difference ($\sigma_{t:w} - \sigma_{t:c}$) used in Eq. 5-31. Note 1 erg = 10^{-7} J.
[b] Results using the equation of Yalkowsky et al. (1976):

Aqueous Solubility

- Example (see Illustrative Example 5.5)
  - What is the solubility of naphthalene in a 20% acetone/water solution at 298 K?

$$\gamma_{il}^{sat}(f_{v,Acet}=0.2)=10^{-\sigma_i^c f_v}\gamma_{Naph,w}^{sat}$$



    - activity coefficient of naphthalene (solid)

$$x_w^{sat}=\frac{1}{\gamma_w^{sat}}\frac{p_s^*}{p_L^*}$$

$$\gamma_w^{sat}=\frac{1}{x_w^{sat}}\frac{p_s^*}{p_L^*}=\frac{1}{C_w^{sat}\overline{V}_w}\frac{p_s^*}{p_L^*}$$

Aqueous Solubility

$$\gamma_w^{sat} = \frac{1}{C_w^{sat}\overline{V}_w}\frac{p_s^*}{p_L^*}$$

- Example
  - activity coefficient of naphthalene (solid)
    - $C_w^{sat} = 10^{-3.60}$ M
    - $V_w = 0.018$ L mol^{-1}
    - vapor pressure ratio

$$\ln\frac{p_{iS}^*}{p_{iL}^*} = -(6.80 + 1.1\tau - 2.3\log\sigma)\left(\frac{T_m}{T} - 1\right)$$

Aqueous Solubility

$$\gamma_w^{sat} = \frac{1}{C_w^{sat}\overline{V}_w}\frac{p_s^*}{p_L^*}$$

- Example
  - activity coefficient of naphthalene (solid)
    - vapor pressure ratio

$$\ln\frac{p_{iS}^*}{p_{iL}^*} = -(6.80 + 1.1\tau - 2.3\log\sigma)\left(\frac{T_m}{T} - 1\right)$$

      - τ = 0 (no *SP3*, no *SP2*, 1 *RING*)
      - σ = 4 (2 planes of rotational symmetry)
      - T_m = 80.2 °C = 353.4 K

$$\ln\frac{p_{iS}^*}{p_{iL}^*} = -(6.80 + 1.1(0) - 2.3\log(4))\left(\frac{353.4}{298.2} - 1\right) \Rightarrow \frac{p_{iS}^*}{p_{iL}^*} = 0.37$$

Aqueous Solubility

$$\gamma_{il}^{sat}(f_{v,Acet}=0.2)=10^{-\sigma_i^c f_v}\gamma_{Naph,w}^{sat}$$

- Example
  - activity coefficient of naphthalene (solid)

$$\gamma_w^{sat}=\frac{1}{(10^{-3.60})(0.018)}(0.37)=81{,}800$$

  - $\sigma_i^c = 6.5$ (Table 5.8)
  - $f_v = 0.2$

$$\gamma_{il}^{sat}(f_{v,Acet}=0.2)=10^{-(6.5)(0.2)}(81{,}800)$$

$$\gamma_{il}^{sat}(f_{v,Acet}=0.2)=(0.050)(81{,}800)$$

$$\gamma_{il}^{sat}(f_{v,Acet}=0.2)=4{,}100$$

Aqueous Solubility

- Example
  - solubility: naphthalene in 20% acetone/water

$$C_{naph,l}^{sat} = \frac{1}{\gamma_{naph,l}^{sat}(f_{v,acet} = 0.2)\overline{V}_w} \frac{p_s^*}{p_L^*}$$

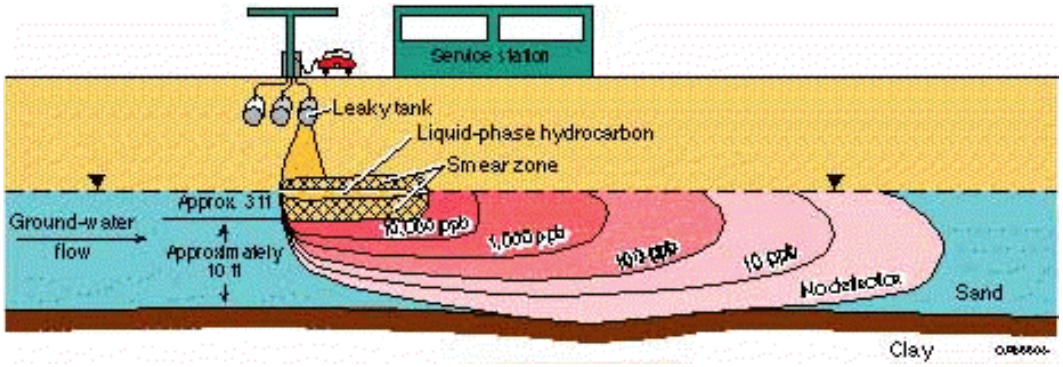
$$C_{naph,l}^{sat} = \frac{1}{(4{,}100)(0.018)}(0.37)$$

$$C_{naph,l}^{sat} = 10^{-2.30}\ \mathrm{M}$$

$$C_w^{sat} = 10^{-3.60}\ \mathrm{M}$$

Aqueous Solubility

- Organic liquid mixtures
  - petroleum – gasoline, oil, kerosene
  - coal tar
  - PCBs – Arochlor



Aqueous Solubility

- At equilibrium

$$\mu_{\text{organic mix}} = \mu_0 + RT \ln \gamma_{\text{organic mix}} x_{\text{organic mix}}$$

  - $\gamma_{org\ mix} \approx 1$ to 5
  - $x_{org\ mix}$
    - need *average* mw of organic liquid mixture
    - e.g., coal tar 150 g mol^{-1}
  - no melting costs
    - compound is already in liquid phase in organic mixture

$$\mu_{org\ mix} = \mu_w$$

$$\gamma_{org\ mix} x_{org\ mix} = \gamma_w x_w$$

$$x_w = \frac{\gamma_{org\ mix} x_{org\ mix}}{\gamma_w}$$

$$C_w = \frac{\gamma_{org\ mix} x_{org\ mix}}{\gamma_w \overline{V}_w}$$