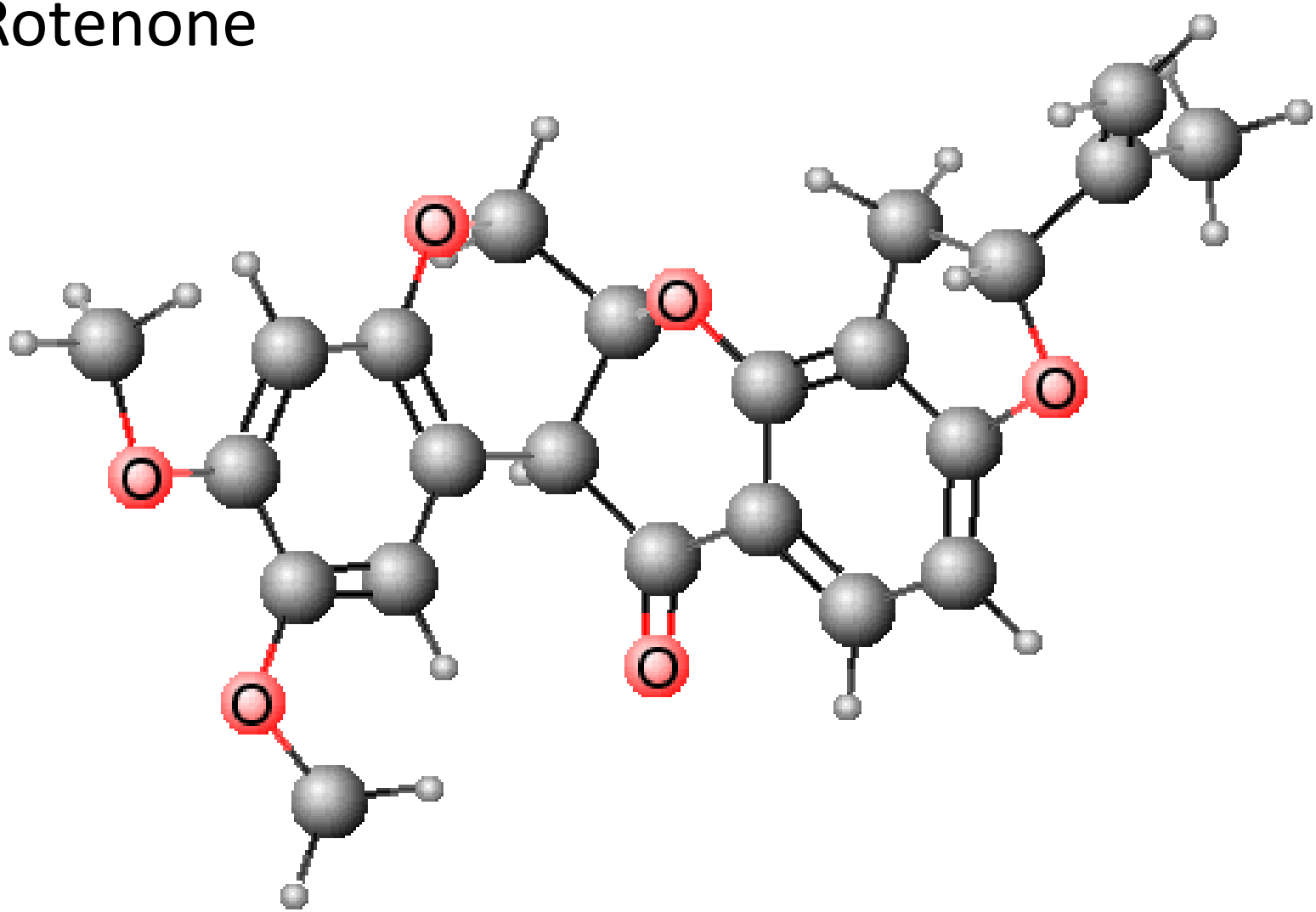
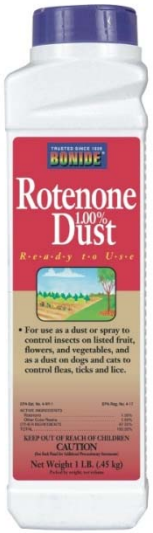
# Interesting molecule of the day

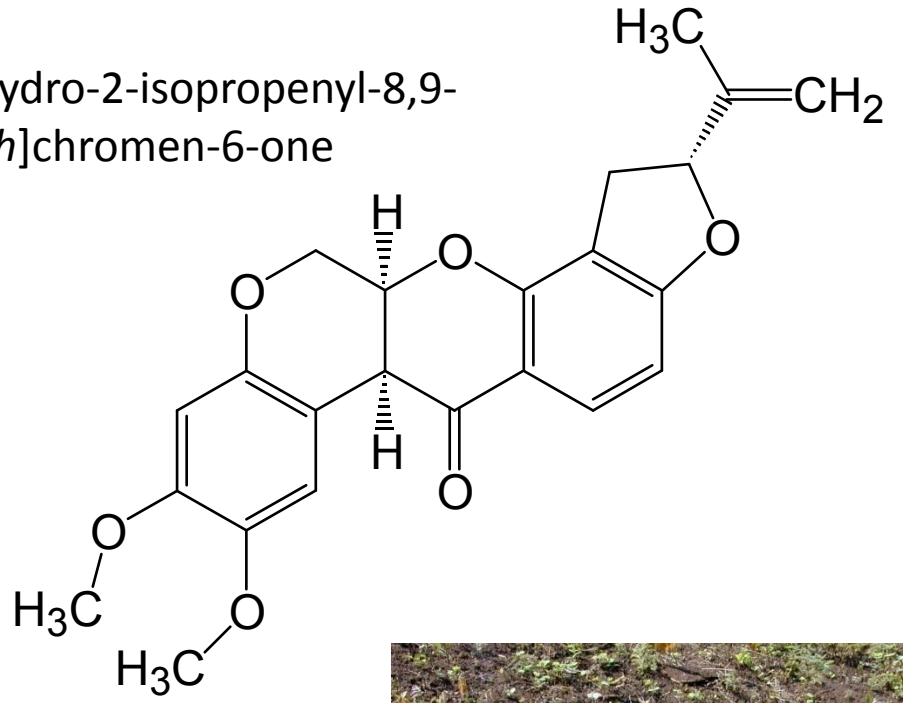
- Rotenone



# Interesting molecule of the day

- Rotenone (an “isoflavone”)
  - $C_{23}H_{22}O_6$
  - (2*R*,6a*S*,12a*S*)-1,2,6,6a,12,12a-hexahydro-2-isopropenyl-8,9-dimethoxychromeno[3,4-*b*]furo[2,3-*h*]chromen-6-one
  - uses
    - pesticide
    - insecticide
    - eradication of exotic (non-native) fish
      - extracted from plants, used to catch fish
    - allowed for use on organic produce
      - USDA: “non-synthetic”




# Interesting molecule of the day

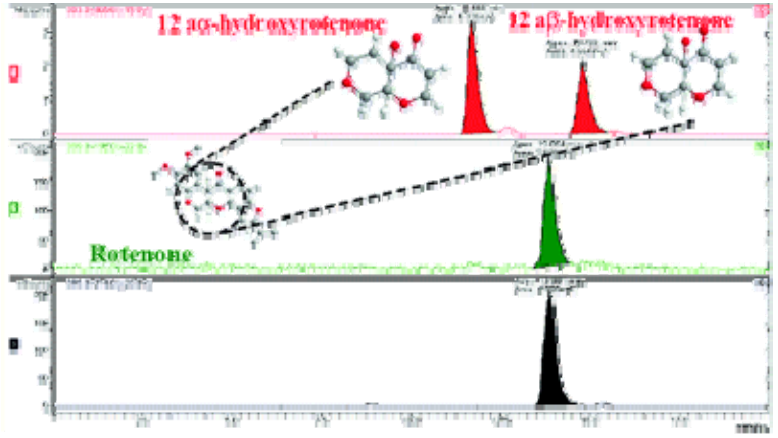
- Rotenone in the news
  (Billings Gazette, Jan 15, 2008)
  - project to remove non-native fish
    - replace with westslope cutthroat trout
  - poisoning of fish in 21 lakes in Montana
  - Montana Fish, Wildlife, and Parks cited environmental concerns
    - U.S. Fish and Wildlife Service approves
  - state commissioners voted to go ahead

# Interesting molecule of the day

- Rotenone
  - toxicity
    - mild toxicity for humans, animals
      - 143 mg $kg^{-1}$ (child)
      - may be related to Parkinson's Disease
    - high toxicity for fish
      - easily absorbed through gills
      - not absorbed through skin or ingestion
  - toxicity method
    - interferes with electron transport in mitochondria
    - prevents NADH from being converted into ATP

# Interesting molecule of the day

- Rotenone
  - persistence
    - half-life of a few hours to several weeks
    - degradation mainly by photolysis
    - breakdown to non-toxic products
  - readily absorbed
    - soils
    - suspended sediment



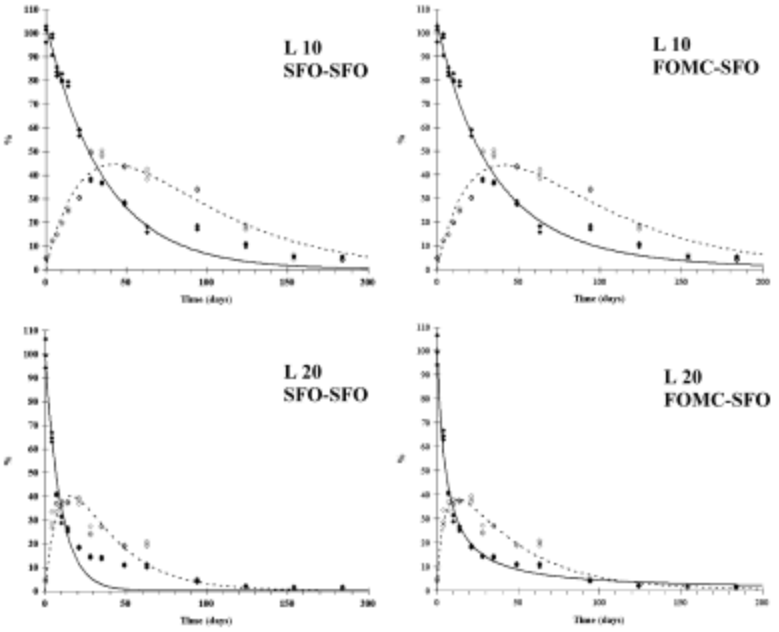




Figure 4. Experimental data of rotenone degradation (●) and ROT-OH formation and degradation (○) in L soil at two different temperatures. SFO and FOMC, for rotenone (—) and ROT-OH (- - -).

Cavoski et al. (2008) *J. Agric. Food Chem.* **55**(17), 7069-7074

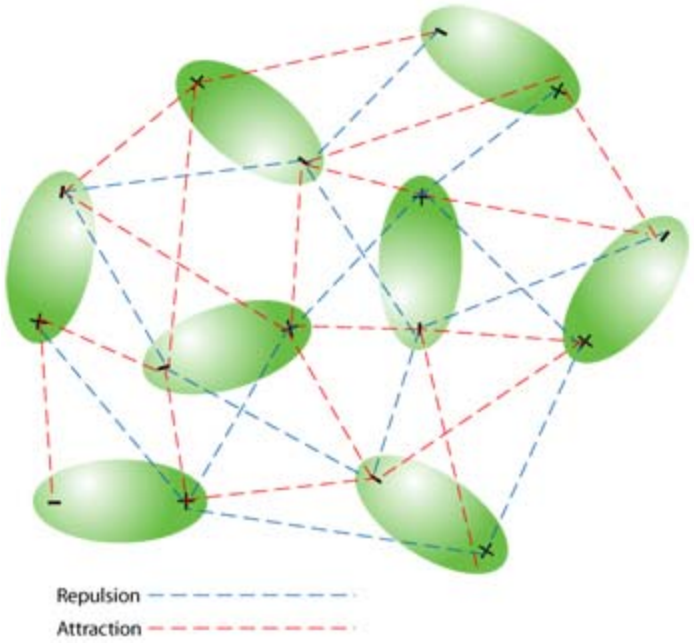
# Interesting molecule of the day

Rotenone Lake Davis

- Trout come back

# Molecular interactions = thermodynamics

- Partition
  - breaking and making of "bonds" during phase change
- Origins of intermolecular interactions
  - non-specific
    - London dispersive energies
    - Debye energies
    - Keesom energies
  - specific
    - polar;
      a.k.a., electron donor-acceptor

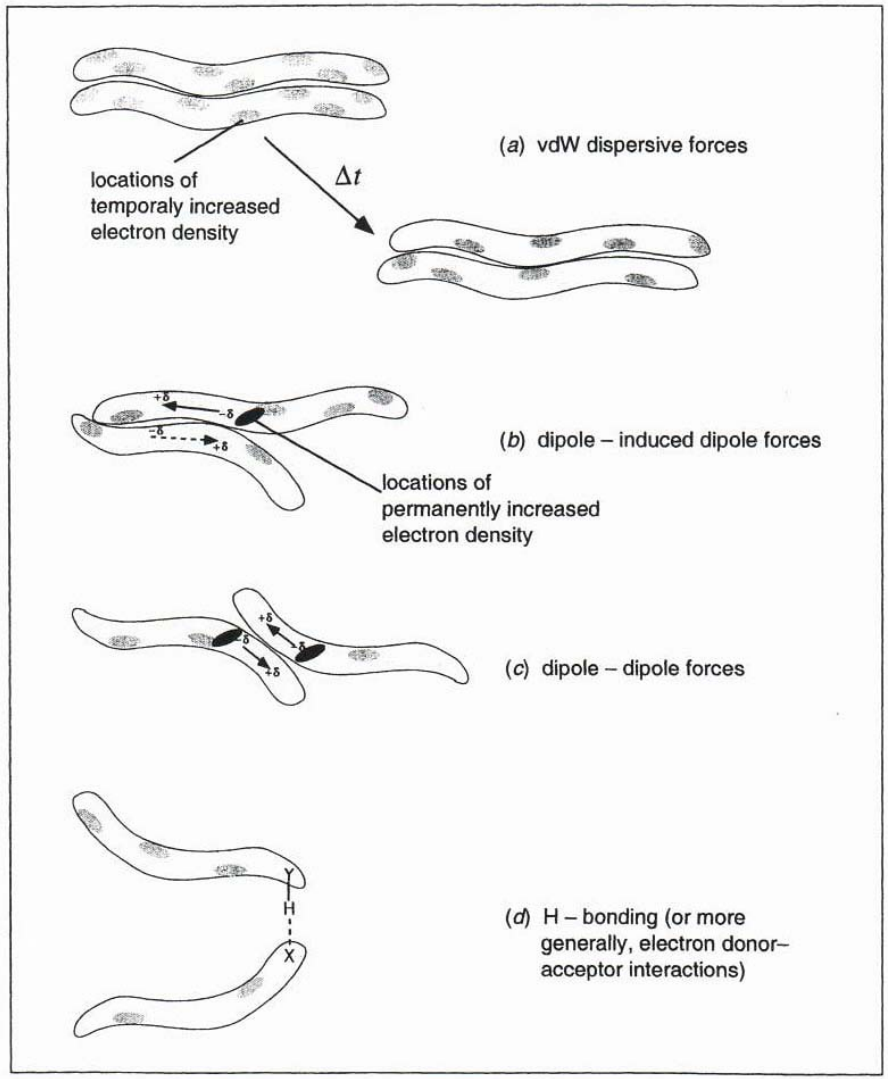


# Molecular interactions = thermodynamics

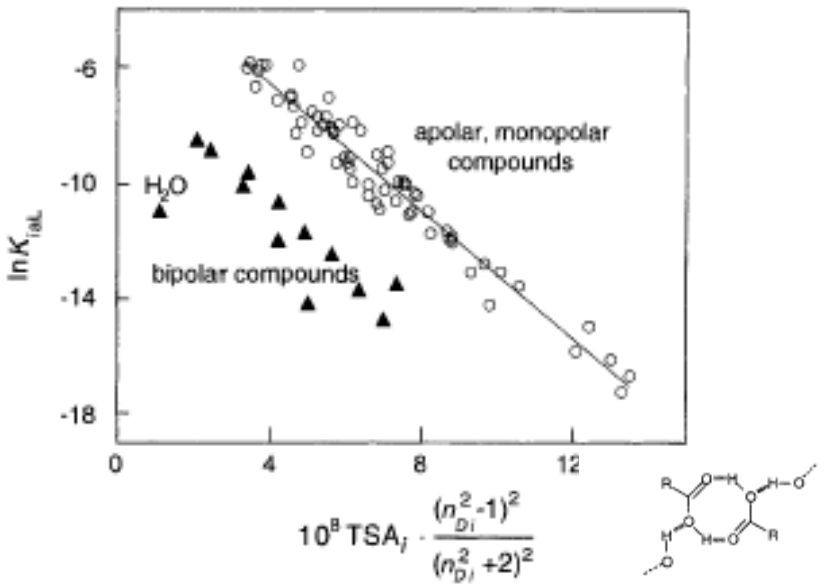
- Absorption (in between)
  - A:*i*:A + B:B ↔ A:A + B:*i*:B
- Adsorption (surface or interface)
  - A:*i*:A + A:B ↔ A:A + A:*i*:B

- Intermolecular attractions (Uncharged molecules)
- Non-specific (vdW)
- Uneven electronic distributions (London)
- Dipole-induced (Debye)
- Dipole-Dipole (Keesom)
- Specific (H bonding)

# Molecular interactions = thermodynamics

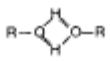



$$\Delta_{disp}G \,/\, \mathrm{J\ mol^{-1}} \approx -\text{constant}\,(\mathrm{TSA}_i)\left[\frac{n_{Di}^2-1}{n_{Di}^2+2}\right]\left[\frac{n_{Di}^2-1}{n_{Di}^2+2}\right]$$





carboxylic acids


alcohols

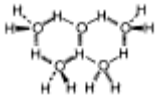

water

**Figure 3.5** H-bonding in various pure liquids.

# Equilibrium Partition Constants

A:*i*:A ↔ + B:*i*:B

Reactant ↔ Product

At equilibrium

K *i*(AB) = Concentration in B/Concentration in A

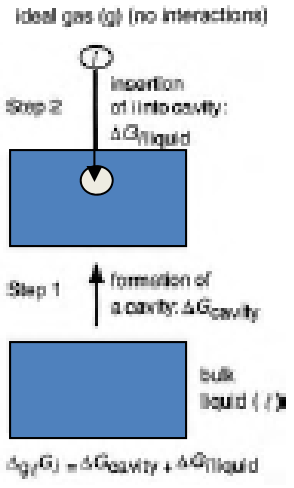



Figure 3.2 Absorption of a compound *i* from an ideal gas phase into a bulk liquid.

$$K_{iAB} = \text{constant} \bullet e^{-\Delta_{AB}G_i / RT}$$

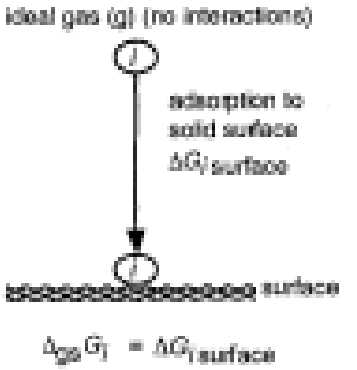
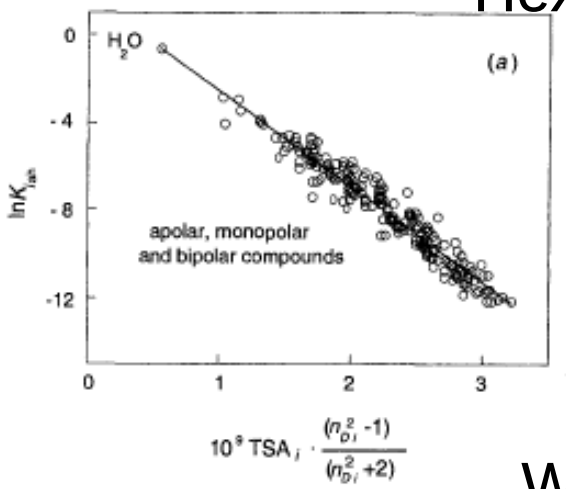


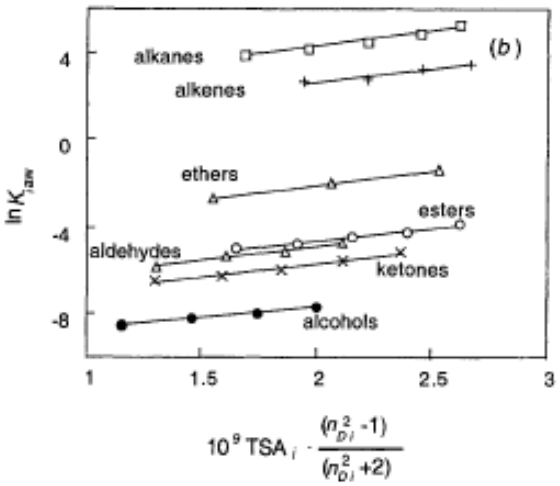

Figure 3.3 Adsorption of a compound *i* from an ideal gas phase to a surface.

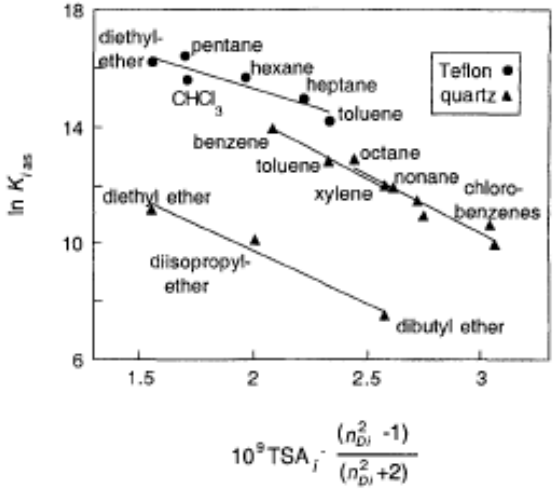
# Air solvent partition/ Air solid partition

Hexadecane

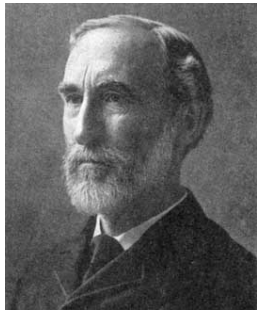



Water



J.W. Gibbs



# Thermodynamics

- What is chemical potential?
  - Chemical potential is the (  ) free energy added for each added mole of a component (*i* ) of the system

$$\mu_i \quad (\mathrm{J\,mol^{-1}}) \equiv \left[\frac{\partial G}{\partial n_i}\right]_{T,P,n_{j\neq i}} \quad \begin{matrix}(\mathrm{J}) \\ (\mathrm{mol})\end{matrix}$$

$$\mu_i \equiv G_i = H_i - TS_i$$

# Thermodynamics

- What is enthalpy?
  - The enthalpy of a molecule is a measure of the molecule's attractions to
    - its surroundings (*inter*molecular)
    - itself (*intra*molecular)

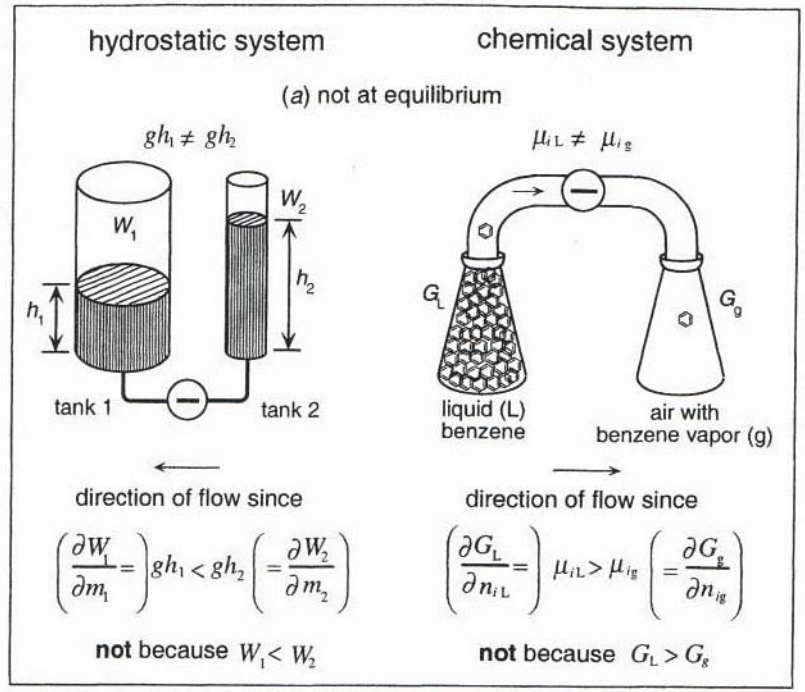
$$H$$

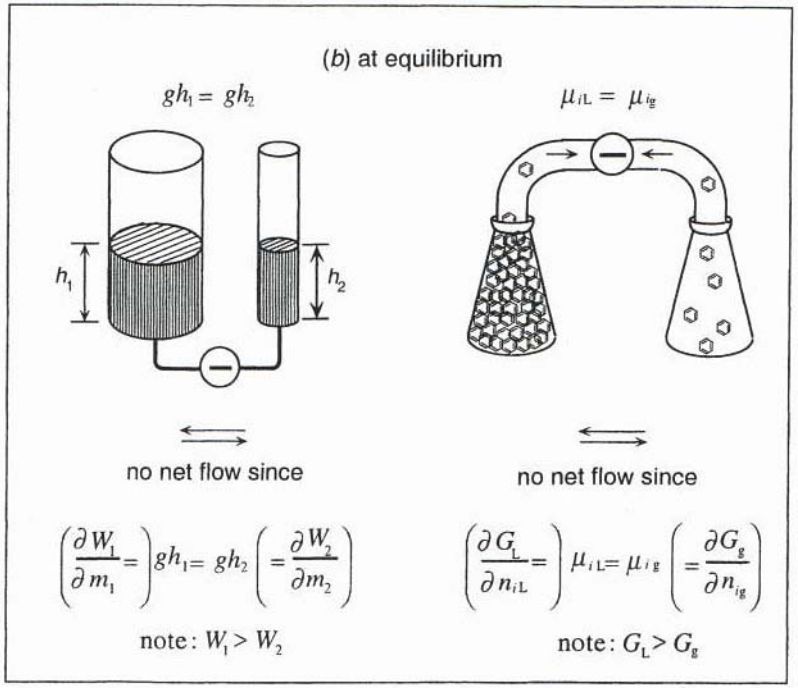
# Thermodynamics

- What is entropy?
  - The entropy of a molecule is its freedom to
    - twist and turn (*orientation*)
    - move electrons around its structure (*configuration*)
    - be “random” in space (*translation*)

$$S$$

# Hydrostatic system



# Thermodynamics

G.N. Lewis

- What is *fugacity*?
  - A measure of chemical potential
  - A tendency to "*flee*"
  - A change in chemical potential related to a change in vapor pressure ($dp_i$)

$$(d\mu_i)_T = \frac{V}{n_{ig}} dp_i$$

# Thermodynamics

- What is fugacity?
  - Assuming an ideal gas…

$$p_i V = n_i RT \qquad \frac{V}{n_i} = \frac{RT}{p_i}$$

  - …and integrating with respect to some standard state ($\mu_i^0$, $p_i^0$),

$$\mu_i = \mu_i^0 + RT \ln\left[\frac{p_i}{p_i^0}\right]$$

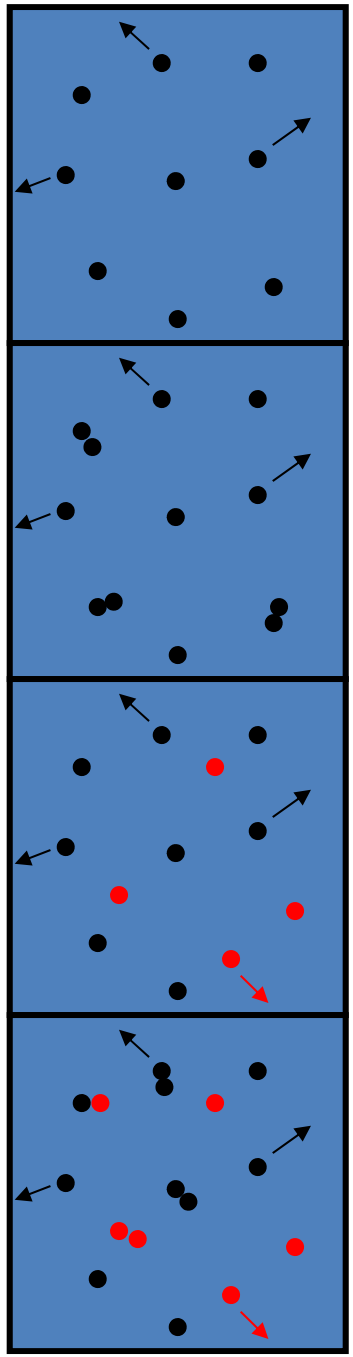
# Thermodynamics

- Fugacity of non-ideal gases
  - higher concentrations
  - intermolecular interactions
  - gas mixtures

$$\mu_i = \mu_i^0 + RT \ln \left[ \frac{f_i}{p_i^0} \right]$$

# Thermodynamics

- Ideal gas: $f_i = p_i = p$
- Non-ideal gas: $f_i = \theta_i p_i = \theta_i p$
- Ideal gas mixture: $f_i = x_i p$
- Non-ideal gas mixture: $f_i = \theta_i x_i p$



# Thermodynamics

- Fugacity at the standard state
  - standard state:
    - reference state at standard conditions (STP)
    - $T$ = 25°C (298.2 K)
    - $p$ = 1 bar (0.987 atm)
  - for gases: ***pure gas*** at STP
  - for liquids: ***pure liquid*** at STP
  - for solids: ***pure solid*** at STP

# Thermodynamics

- Fugacity of liquids, ideal and non-ideal

$$\mu_i = \mu_i^0 + RT \ln\left[\frac{f_i}{f_i^*}\right]$$

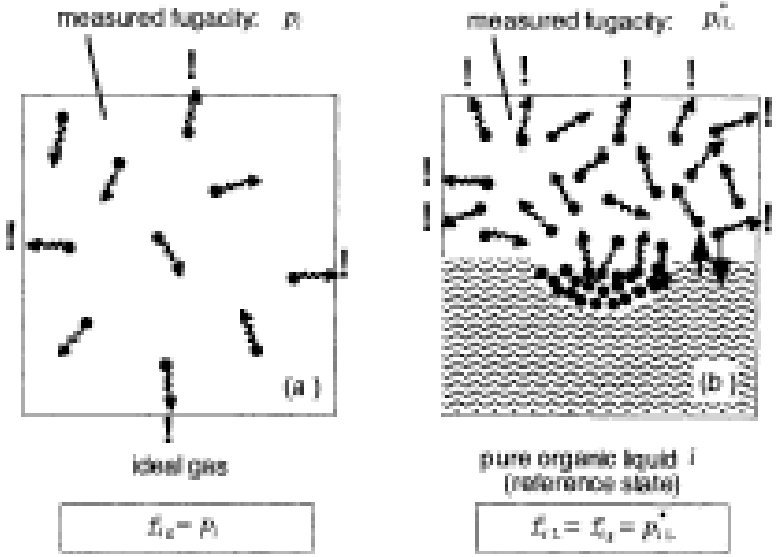
the liquid's fugacity at STP…

$$= \mu_i^0 + RT \ln\left[\frac{f_i}{p_{iL}^*}\right]$$

… is the vapor pressure of the liquid at STP

# Thermodynamics

- Ideal liquid: $f_i = p^*_{iL}$ the liquid's vapor pressure at STP
- Non-ideal liquid: $f_i = \gamma_i p^*_{iL}$
- Ideal liquid mixture: $f_i = x_i p^*_{iL}$
- Non-ideal liquid mixture: $f_i = \gamma_i x_i p^*_{iL}$


measured fugacity: $p_i$
(a)
ideal gas
$f_{i,a} = p_i$
measured fugacity: $p_{i,L}^{*}$
(b)
pure organic liquid $i$
(reference state)
$f_{i,L} = f_{i,s} = p_{i,L}^{*}$
measured fugacity: $x_{i,l} \cdot p_{i,L}^{*}$
(c)
ideal liquid solution of $i$ (•) in $j$ (○)
$f_{i,l} = f_{i,g} = x_{i,l} \cdot p_{i,L}^{*}$
measured fugacity: $\gamma_{i,l} \cdot x_{i,l} \cdot p_{i,L}^{*}$
(d)
nonideal liquid solution of $i$ (•)
in e.g., water (○)
$f_{i,l} = f_{i,g} = \gamma_{i,l} \cdot x_{i,l} \cdot p_{i,L}^{*}$

# Thermodynamics

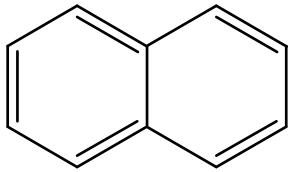
- Fugacity of solids, ideal and non-ideal

$$\mu_i = \mu_i^0 + RT \ln\left[\frac{f_i}{f_i^*}\right]$$

the solid's fugacity at STP…

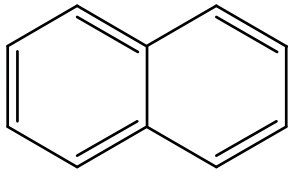
$$= \mu_i^0 + RT \ln\left[\frac{f_i}{p_{iS}^*}\right]$$

… is the vapor pressure of the solid at STP

# Thermodynamics

- Ideal solid: $f_i = p^*_{iS}$ the solid's vapor pressure at STP
- Non-ideal solid: $f_i = \gamma_i p^*_{iS}$
- Ideal solid mixture: $f_i = x_i p^*_{iS}$
- Non-ideal solid mixture: $f_i = \gamma_i x_i p^*_{iS}$

# Thermodynamics

- Gases:

$$\mu_i = \mu_i^0 + RT \ln\left[\frac{f_i}{p_i^0}\right] = \mu_i^0 + RT \ln\left[\frac{\theta_i x_i p_i^0}{p_i^0}\right]$$

$$= \mu_i^0 + RT \ln\left[\theta_i x_i\right]$$

- Liquids:

$$\mu_i = \mu_i^0 + RT \ln\left[\frac{\gamma_i x_i p_{iL}^*}{p_{iL}^*}\right] = \mu_i^0 + RT \ln\left[\gamma_i x_i\right]$$

- Solids:

$$\mu_i = \mu_i^0 + RT \ln\left[\frac{\gamma_i x_i p_{iS}^*}{p_{iS}^*}\right] = \mu_i^0 + RT \ln\left[\gamma_i x_i\right]$$

# Thermodynamics

*ideal* *nonideal*

$$\mu_i = \mu_i^0 + RT \ln\left[\theta_i x_i\right]$$

$$\mu_i = \mu_i^0 + RT \ln\underbrace{\left[\gamma_i x_i\right]}_{a_i}$$

$a_i$ *activity*

# Partition coefficients that we will see later

**Table 3.6** Examples of Simple One-Parameter Linear Free Energy Relationships (LFERs) for Relating Partition Constants and/or Partition Coefficients in Different Two-Phase Systems (Including the Pure Compound as Phase)

| Partition Constants/Coefficients Correlated | LFER | Discussed in Chapter |
|---|---|---|
| Octanol–water partition constant and aqueous solubility of the pure liquid compound | $\log K_{iow} = -a \cdot \log C_{iw}^{sat} + b$ | 7 |
| Natural organic carbon–water partition coefficient and octanol–water partition constant | $\log K_{ioc} = a \cdot \log K_{iow} + b$ | 9 |
| Lipid–water partition coefficient and octanol–water partition constant | $\log K_{ilipw} = a \cdot \log K_{iow} + b$ | 10 |
| Air–solid surface partition constant and vapor pressure of the pure liquid compound | $\log K_{ias} = a \cdot \log p_{iL}^{*} + b$ | 11 |
| Air–particle partition coefficient and air–octanol partition constant | $\log K_{iap} = a \cdot \log K_{iao} + b$ | 11 |