Interesting molecule of the day

- Rotenone
Interesting molecule of the day

- Rotenone (an “isoflavone”)
  - $C_{23}H_{22}O_6$
  - $(2R,6aS,12aS)-1,2,6,6a,12,12a$-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”
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 (--).

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)
  - $A:i:A + B:B \leftrightarrow A:A + B:i:B$

- Adsorption (surface or interface)
  - $A:i:A + A:B \leftrightarrow A:A + A:i:B$

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

(a) vDW dispersive forces
locations of temporarily increased electron density

(b) dipole – induced dipole forces
locations of permanently increased electron density

(c) dipole – dipole forces

(d) H – bonding (or more generally, electron donor-acceptor interactions)

\[
\Delta_{\text{disp}} G / J \text{ mol}^{-1} = -\text{constant} \left( \text{TSA}_i \right) \left[ \frac{n_i^2 - 1}{n_D^2 + 2} \right] \left[ \frac{n_i^2 - 1}{n_D^2 + 2} \right]
\]

Figure 3.5 H-bonding in various pure liquids.
Equilibrium Partition Constants

A: \( i \cdot A \leftrightarrow + B: i \cdot B \)

Reactant ↔ Product

At equilibrium

\[ K_{i(AB)} = \text{Concentration in B/Concentration in A} \]

\[ K_{iAB} = \text{constant} \cdot e^{-\Delta_{AB}G_i/RT} \]
Air solvent partition/ Air solid partition

Hexadecane

Water
Thermodynamics

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

\[
\mu_i \quad (\text{J mol}^{-1}) \equiv \left[ \frac{\partial G}{\partial n_i} \right]_{T,P,n_j \neq i} \quad (\text{J})
\]

\[
\mu_i \equiv G_i = H_i - TS_i
\]
Thermodynamics

• What is enthalpy?
  • The enthalpy of a molecule is a measure of the molecule’s attractions to
    • its surroundings (intermolecular)
    • itself (intramolecular)
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

(a) not at equilibrium

- $gh_1 < gh_2$ (not because $W_1 < W_2$)
- $\frac{\partial W}{\partial m_1} = gh_1 < gh_2 = \frac{\partial W}{\partial m_2}$
- $\mu_{L1} > \mu_{i2}$ (not because $G_L > G_s$)

(b) at equilibrium

- $gh_1 = gh_2$
- $\frac{\partial W}{\partial m_1} = gh_1 = gh_2 = \frac{\partial W}{\partial m_2}$
- $\mu_{L1} = \mu_{i2}$

- no net flow since
- $W_1 > W_2$
- note: $G_L > G_s$

chemical system

- liquid (L) benzene
- air with benzene vapor (g)

- $\mu_{L1} = \mu_{i2}$
Thermodynamics

• 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...

\[ p_i V = n_i RT \]

\[ \frac{V}{n_i} = \frac{RT}{p_i} \]

• ...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)
    • $T = 25^\circ C$ (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: $p_i$

ideal gas

$f_i = p_i$

pure organic liquid $i$ (reference state)

$f_i = f_L = p_L$

measured fugacity: $x_i \cdot p_L$

ideal liquid solution of $i$ ($\bullet$) in $j$ ($\circ$)

$f_i = f_L = x_i \cdot p_L$

measured fugacity: $y_i \cdot x_i \cdot p_L$

nonideal liquid solution of $i$ ($\bullet$) in e.g. water ($\circ$)

$f_i = f_L = y_i \cdot x_i \cdot p_L$
Thermodynamics

• Fugacity of solids, ideal and non-ideal

\[
\mu_i = \mu^0_i + RT \ln \left( \frac{f_i}{f_i^*} \right)
\]

the solid’s fugacity at STP...

\[
= \mu^0_i + RT \ln \left( \frac{f_i}{p_{iS}} \right)
\]

... is the vapor pressure of the solid at STP.
Thermodynamics

• Ideal solid:
  \[ f_i = p_{is}^* \]

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

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

- **Solids:**
  \[ \mu_i = \mu_i^0 + RT \ln \left[ \frac{\gamma_i x_i p_i^*}{p_{iS}^*} \right] = \mu_i^0 + RT \ln [\gamma_i x_i] \]
Thermodynamics

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

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

activity \( a_i \)
Partition coefficients that we will see later

<table>
<thead>
<tr>
<th>Partition Constants/Coefficients Correlated</th>
<th>LFER</th>
<th>Discussed in Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octanol–water partition constant and aqueous solubility of the pure liquid compound</td>
<td>( \log K_{\text{fw}} = -a \cdot \log C_{\text{sat}}^{\text{fw}} + b )</td>
<td>7</td>
</tr>
<tr>
<td>Natural organic carbon–water partition coefficient and octanol–water partition constant</td>
<td>( \log K_{\text{roc}} = a \cdot \log K_{\text{fw}} + b )</td>
<td>9</td>
</tr>
<tr>
<td>Lipid–water partition coefficient and octanol–water partition constant</td>
<td>( \log K_{\text{lipw}} = a \cdot \log K_{\text{fw}} + b )</td>
<td>10</td>
</tr>
<tr>
<td>Air–solid surface partition constant and vapor pressure of the pure liquid compound</td>
<td>( \log K_{\text{ias}} = a \cdot \log \rho_a + b )</td>
<td>11</td>
</tr>
<tr>
<td>Air–particle partition coefficient and air–octanol partition constant</td>
<td>( \log K_{\text{iap}} = a \cdot \log K_{\text{iao}} + b )</td>
<td>11</td>
</tr>
</tbody>
</table>

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)