

## Environmental Chemodynamics

Principles of Environmental Toxicology  
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## Learning Objectives

- List the thermodynamic functions used to describe the energy status of molecules in an environmental system.
- Understand the relationship of Gibb's free energy and chemical potential in the transfer or transformation of chemicals in a system.
- Develop a basic understanding of fugacity and its role in environmental transformations.
- Define activity and its relationship to concentration.

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## Learning Objectives, 2

- Understand the concept of energy bookkeeping and the relationship of Gibb's free energy to enthalpy and entropy in an phase transformation or chemical reaction.
- Develop a basic understanding of first order and psuedo-first order chemical kinetics including integrated rate expressions, half-lives and T dependence.

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## Learning Objectives, 3

- Understand the compartment model of the ecosphere.
- Understand the partitioning of chemicals and how partition constants are used in describing environmental systems.
- Understand the basic approaches to modeling chemodynamics and the usefulness and limitations of model use.

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## Environmental Chemodynamics

- Thermodynamics and kinetics of processes are important in a description of the fate and transport of environmental chemicals.
  - Dynamics and energy balance drive the system.
  - Phase transfer and chemical reaction dynamics.
  - Interfacial and inter-compartment transport.



## Thermodynamics

- The study of systems at equilibrium.
  - Reversible processes.
- Used to describe the energy status of molecules in an environmental system.
- Thermodynamic functions.
  - Chemical potential,  $\mu$ .
  - Fugacity,  $f$ .
  - Activity coefficient,  $a$ .
  - Gibbs free energy,  $G$ .
  - Enthalpy,  $H$ .
  - Entropy,  $S$ .

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## Chem. Potential & Gibbs Free Energy

- Molecules have internal energies (vibration, rotation, etc.) and external energy (translation, interaction, etc.).
- Energy depends on temperature, pressure and chemical composition.
- Energy content of a chemical is a population concept - Population of the chemical and all of the other substances present (total free energy).

## $\mu, G$

- Chemical potential is the incremental energy (as additional molecules) added to the total free energy of the system.

$$\left[ \frac{\partial G(kJ)}{\partial n_i(mol)} \right]_{T,P,n_{j \neq i}} \equiv \mu_i (kJ \cdot mol^{-1})$$

$$G(P, T, n_1, n_2, \dots, n_i) = \sum_i n_i \mu_i$$

## Reference, Standard States

- Spontaneous transfer of chemical and thermal energy will occur until equilibrium is reached.
- Chemical potential,  $\mu_i$  can be used to quantify the tendency of compound  $i$  to transform or transfer to another system.
  - Absolute values for  $\mu_i$  cannot be calculated but changes from reference states can be.
  - Reference state (e.g. infinite dilution, pure liquid) and standard conditions (P, T) yield a standard chemical potential,  $\mu_i^0$  as a point of comparison for starting and final states of molecular change for  $i$ .

## Fugacity

- Fugacity,  $f$  the fugitive property (fleeing tendency). The fugacity of a gas in a mixture is approximated by its partial pressure.

$$f_i = \theta_i x_i P$$

then,  $f_i \approx P_i$  (since  $\theta_i \approx 1$ )

where:  $f_i$  = fugacity of gas  $i$

$\theta_i$  = fugacity coefficient of gas  $i$

$$x_i = \text{mole fraction of gas } i = \frac{n_i}{\sum_j n_j}$$

10  $P_i$  = partial pressure of gas  $i$

## Fugacity of Liquids and Solids

- Liquids and solids have vapor pressures and the "fleeing tendency" should be related.

$$f_{i \text{ pure liquid}} = \gamma_{i \text{ pure liquid}} \cdot P_i^0(l)$$

$$f_{i \text{ pure solid}} = \gamma_{i \text{ pure solid}} \cdot P_i^0(s)$$

where  $\gamma_i$  = activity coefficient (accounts for non - ideal behavior)

$P_i^0$  = reference state vapor pressure of  $i$ , hence :

$$f_i = \gamma_i \cdot x_i \cdot f_{i \text{ pure liquid(solid)}} \text{ and}$$

$$f_i = \gamma_i \cdot x_i \cdot P_{i \text{ pure liquid(solid)}}^0$$

For ideal liquids,  $\gamma_i = 1$ , and for water,  $\gamma_i \neq 1$ .

## Activity

- Activity: how active a compound is in a given state (e.g. solution, T, P), compared to a reference state (e.g. pure liquid, T, P).
- Activity,  $a_i$  is an "apparent concentration".

$$a_i = \gamma_i \cdot x_i = \frac{f_i}{f_{\text{ref}}}$$

where  $a_i$  = activity,  $\gamma_i$  = activity coefficient and  $x_i$  = mole fraction of  $i$ .

## Enthalpy and Entropy

- Enthalpy,  $h_i$  and entropy,  $s_i$  contribute to  $\gamma_i$  since they describe the non-ideal, molecule-to-molecule interactions in a system.
- Enthalpy (heat energy) is the sum of intramolecular and intermolecular forces for a molecule.
- Entropy (freedom) is the contribution to free energy of a molecule by its randomness of configuration, orientation and translation.

## Energy Bookkeeping

- Molecular change in the environment, such as phase changes (e.g., volatilization) and chemical reaction require energy change.

$$g_i(\text{J/mol}) = h_i - T(\text{K}) \cdot s_i(\text{J/molK}) = \mu_i$$

- Hence, we can calculate molar free energy changes,  $\Delta G$  for environmental processes.
  - Can determine if it will be spontaneous ( $-\Delta G_{\text{rxn}}$ ), or what the energy costs will be.
  - Can estimate equilibrium concentrations.

## Chemical Kinetics

- The study of systems whose chemical composition or energy is changing with time.
- Thermodynamics allows prediction of whether an environmental process will take place, but yields no information about its speed.
- Reaction of atmospheric oxygen and nitrogen with seawater:  
 $2\text{H}_2\text{O} + 2\text{N}_2 + 5\text{O}_2 \rightarrow 4\text{HNO}_3$  (0.1M)  
 $\Delta G_{298}^0 = -355 \text{ kJ/mol}$   
 – Fortunately, immeasurably slow!

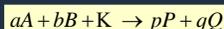
## Reaction Pathway

- The mechanism of a reaction includes all of the individual steps along the pathway of reactants to products.
- The rate of the reaction (how fast) may be limited by any one of these steps.
- Molecular properties of reactants and products allow calculation of equilibrium constants for a reaction, but not rate constants.
  - Experimentally determined.

## Rate of Reaction

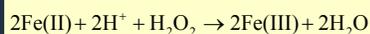
- Rate of reaction of chemicals is a function of several variables.
  - Chemical composition, T, P, or V.

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$$\text{Rate} = \mathfrak{R} \left( \frac{\text{moles}}{\text{liter} \cdot \text{sec}} \right) = -\frac{1}{a} \frac{d(A)}{dt} = -\frac{1}{b} \frac{d(B)}{dt} = \frac{1}{p} \frac{d(P)}{dt} = \frac{1}{q} \frac{d(Q)}{dt}$$

Example: Fenton's reaction



$$\mathfrak{R} = -\frac{d[\text{H}_2\text{O}_2]}{dt} = -\frac{1}{2} \frac{d[\text{Fe(II)}]}{dt}$$

## Concentration Dependence

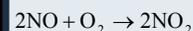
- Most often, the concentration dependence of reaction rates takes a simple form.

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$$\mathfrak{R} = k(A)^\alpha (B)^\beta \Lambda$$

where (A), (B) are concentrations of reactants, exponents  $\alpha, \beta$  are the order of reaction with respect to A and B, and  $k$  is the rate constant.

Example:



$$\mathfrak{R} = \frac{d(\text{NO}_2)}{2dt} = k(\text{NO})^2 (\text{O}_2)$$



## Integrated Rate Expressions

- Many chemical reactions in the environment follow first order or *pseudo*-first order ( $B \gg A$ ) chemical kinetics.

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$$-\frac{d(A)}{dt} = k(A)$$

Upon integration :

$$\ln \frac{(A)}{(A)_0} = -kt$$

Hence a plot of  $\ln(A)$  vs.  $t$  will be a line of slope  $k$ .

Pseudo - first order :

$$\ln \frac{(A)_0}{(A)} = -k(B)_0 t$$

## Half-Lives of Reactions

- Useful because it gives a feeling for the time scale of the reaction.
- Found by inserting  $(A) = \frac{1}{2}(A)_0$  into the integrated rate equation.

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$$\text{First order : } t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

$$\text{Pseudo - first order : } t_{1/2} = \frac{\ln 2}{k(B)_0}$$

$$\text{Second order : } t_{1/2} = \frac{1}{2k(A)_0}$$

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## T Dependence of Reaction Rates

- The rate constant of an elementary reaction is empirically found to have a temperature dependence.

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad \text{or} \quad \ln k = \ln A - \left(\frac{E_a}{RT}\right)$$

where  $A$  is the frequency factor or pre - exponential factor.

Hence, a semilog plot of rate constant vs. inverse  $T$  should be a straight line with slope  $E_a/R$  and intercept  $\ln a$ . This is commonly referred to as an Arrhenius plot.

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## Complex Reactions

- Heterogeneous reactions.
  - Surface effects on reactions.
- Competitive reactions.
  - Combinations of elementary reactions using one or more of the same reactants.
- Consecutive reactions.
  - Sequential processes often with one being the rate limiting step.

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## Compartments

- The behavior and effects of environmental pollutants are related to their dynamics in the four major compartments of the ecosphere.
  - Air (atmosphere).
  - Water (hydrosphere).
  - Soil (lithosphere).
  - Biota (biosphere).



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## Environmental Interfaces

- An interface is where two different compartments meet and share a common boundary.
  - Factors in compartment and interfacial dynamics.
    - Physicochemical properties of the chemical.
    - Transport properties in the environment.
    - Chemical transformation.



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### Compartments and Processes

- Air
  - Diffusion and dispersion.
  - Photolysis and oxidation.
  - Heterogeneous reactions on airborne particulates and cloud vapor.



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### Compartments and Processes

- Water
  - Solution, sorption, diffusion, volatilization and bio-uptake.
  - Photolysis, hydrolysis, oxidation, metabolism, biodegradation.



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### Compartments and Processes

- Soil
  - Sorption, runoff, volatilization, leaching, bio-uptake.
  - Hydrolysis, oxidation, reduction, photolysis, metabolism, biodegradation.



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### Compartments and Processes

- Biota
  - Uptake, metabolism, elimination, sequestration, transport, sorption.
  - Decomposition, biotransformation, biodegradation.



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### Env. Processes and Properties

- Physical transport.
  - Meteorological.
    - Wind.
  - Bio-uptake.
    - Biomass and food chain.
  - Sorption
    - Organic content of soil/sediment, aquatic suspensions.
    - Adsorption and chemisorption.

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### Env. Processes and Properties

- Volatilization.
  - Turbulence, wind velocity, evaporation, aeration rate, organic matter.
- Runoff.
  - Precipitation rate.
- Leaching.
  - Adsorption coefficient.
- Fallout.
  - Particulate concentration, wind velocity.

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## Env. Processes and Properties

- Chemical reaction.
  - Photolysis.
    - Solar irradiance, transmissivity of water, air.
  - Oxidation.
    - Concentrations of oxidants and retarders.
  - Hydrolysis.
    - pH, sediment/soil basicity or acidity.
  - Reduction.
    - Oxygen concentration, ferrous ion concentration, oxidation state.

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## Env. Processes and Properties

- Biological.
  - Biotransformation.
    - Microorganism population and acclimation.
    - Biodegradation.
    - Mineralization.

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## Solubility in Water

- Abundance of a chemical per unit volume in the aqueous phase when the solution is in equilibrium with the pure compound (25 °C, 1 atm)
- Saturated solution,  $C_w$  sat.

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## Atmospheric-Water Partitioning

- Equilibrium partitioning of organic chemicals between the gas phase and an aqueous solution.
- Henry's law constant, H or  $K_H$  is the air-water distribution ratio of a dilute solute in pure water.
 
$$K_H = P_i / C_w$$
  - Fugacity implications:
    - high vapor pressure and high fugacity in water should lead to appreciable partition from water to air.

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## O. Solvent-Water Partitioning

- The octanol-water partition coefficient.
  - Why: The distribution of organic compounds between water and natural solids can be viewed as partitioning processes.
  - Biochemical (soil, humics-organic carbon) and biological processes are important pathways.
  - n-Octanol is a surrogate for studying this partitioning (fugacity!).

$$K_{ow} = C_{\text{octanol}} / C_{\text{water}}$$

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## Solid-Water Partitioning

- Adsorption of solute to solid surfaces.
- Freundlich isotherm (constant T).
 
$$C_s = K_F C_w^{1/n}$$
 where  $K_F$  is the Freundlich constant and n is an empirically determined value.
- For  $n \sim 1$ , a distribution coefficient is calculated
 
$$K_d = C_{\text{solid}} / C_{\text{water}}$$

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## Organic Matter-Water Partitioning

- Organic Matter-Water Partition Coefficient,  $K_{om}$ .
- Organic matter consists of large polymeric globular chains.
  - Internal regions are hydrophobic.
- The internal region of the macromolecule becomes “capture” or “solution” regions for neutral or non-polar organic pollutants.

$$K_{om} = C_{\text{organic matter}} / C_{\text{water}}$$

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## Biota-Water Partitioning

- Bioconcentration factor used to describe the partitioning of chemicals between a source (typically water) and biota.
 
$$BCF = C_{\text{organism}} / C_{\text{water}}$$
  - Because bioconcentration is often solvation of non-polar organic chemicals in adipose tissues, it can be viewed as a fat/water partitioning and proportional to similar partitioning constants such as  $K_{ow}$ .
    - Removal of the source will redistribute the chemical (depuration).

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## Chemodynamics - Environmental Systems

- In a compartment model of the ecosphere, chemodynamics can be used in models to better understand the fate and transport of chemicals in the environment.



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## Modeling Concepts

- A model is an imitation of reality which stresses those aspects that are assumed to be important — and omits all properties that are considered to be non-essential (Schwarzenbach).

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## Modeling Strengths

- Mathematical models central in all of science.
- Simplification of complex systems.
- Allows for prediction of chemical behavior.
- Can be used to explain field data and observations.
- Can be used to generate hypotheses.
- Can be used to design experiments.
- Can be modified.
- Allows for development of alternative explanations.

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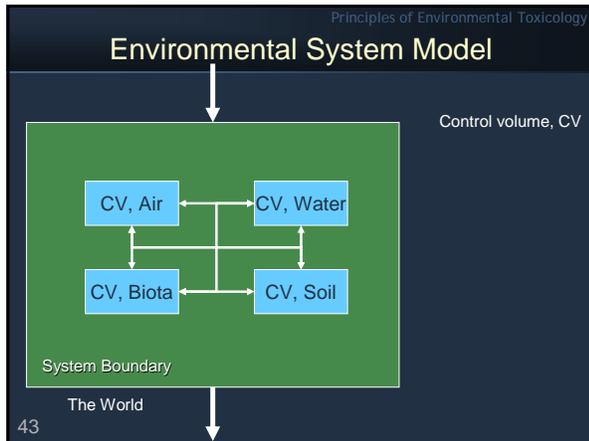
Schwarzenbach

## Modeling Weaknesses

- Over simplification.
- Never as good as real observations and real data.
- Obsolescence.
  - Always subject to “a better model”.



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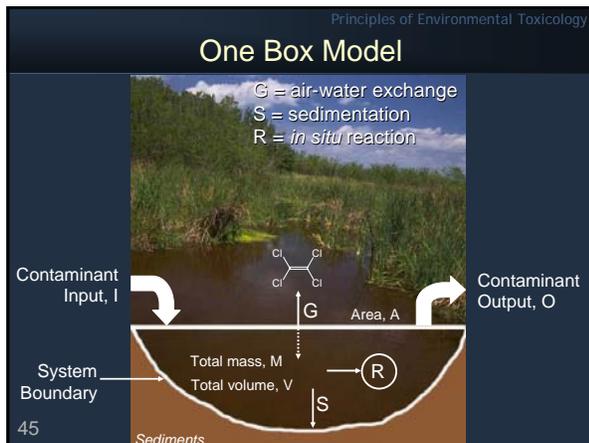
Principles of Environmental Toxicology

## One Box Mass Balance Model

- Example: air-water exchange of perchloroethylene (perc) in a pond fed and drained by a creek.
- Boundary fluxes:
  - $G$  → the exchange of perc between the water and the atmosphere (pond to atmosphere is defined as positive [+]  
flux).
  - $S$  → the net removal of perc to the sediment.
- In situ reaction:
  - $R$  → biodegradation, etc.

$C_2Cl_4$

44 Schwarzenbach



Principles of Environmental Toxicology

## Mass Balance

$$\frac{d(\text{Mass in CV})}{dt} = \Sigma(\text{inputs}) + \Sigma(\text{internal production}) - \Sigma(\text{outputs}) - \Sigma(\text{internal sinks})$$

$$\frac{dM_{\text{perc}}}{dt} = I_{\text{perc}} - O_{\text{perc}} - G_{\text{perc}} - R_{\text{perc}} - S_{\text{perc}}$$

46 Schwarzenbach

- Principles of Environmental Toxicology
- ## Solution for $G$
- $dM/dt = I - O - G - R - S$
  - Assume steady state,  $dM/dt = 0$ .
  - $S, R \ll I, O, G$ .
  - Calculate  $G = I - O$ .
  - Hence, subtracting the output from the input mass<sub>perc</sub> over a time period will yield the estimated net loss of perc to the atmosphere by the system.
- 47 Schwarzenbach

- Principles of Environmental Toxicology
- ## Dynamic Box Models
- Dynamic models needed to describe the effects of system variables that change:
    - $dM/dt \neq 0$ , multiple boxes, random transport, etc.
  - Requires description of system processes.
    - Theories, relationships and data for dynamic transport and transformation processes.
- Example:  $G = A_0 \cdot v_{\text{tot}} \cdot (C_w - C_a/K'_H)$
- $A_0$  = surface area of pond.
  - $v_{\text{tot}}$  =  $a/w$  transfer velocity.
  - $C_{a,w}$  =  $a/w$  concentration.
  - $K'_H$  = Henry's Law constant.
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## Model System Variables

- *In situ* reaction of the chemical.
  - Hydrolysis, photolysis, redox as a function of pH, temperature, light intensity.
- Mass transfer of the chemical at water surface.
  - Wind velocity, temperature.
- Reaction of the chemical in the sediments.
  - Sorption, sequestration, biodegradation, bioturbation.
- Biological uptake, metabolism, sequestration and elimination of the chemical.

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## Model System Variables, 2

- Inlet of contaminants at various depths of the water system.
- Outflow from the water body at the surface and subsurface.
- Mixing of surface water with deeper waters.
- *In situ* production of particulates such as phytoplankton.
- Sorption dynamics of the chemical on suspended, resuspended and settling particulates.

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## Partitioning and Models

- Compartment models require understanding of chemical partitioning, transformations and transport to describe the equilibrium concentration relationships between different compartments.
- An understanding of these relationships allows an understanding and prediction of the dynamics of chemicals in the environment and their eventual fate.

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