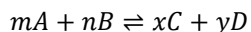


Unit 3: Stability and Change

IMPORTANT EQUATIONS:



Equilibrium constant of gas-phase mixture:

$$K = \frac{p_C^x p_D^y}{p_A^m p_B^n}$$

Equilibrium constant of liquid-phase mixture:

$$K = \frac{[C]^x [D]^y}{[A]^m [B]^n}$$

Reaction quotient...

$$Q = \frac{[C]_t^x [D]_t^y}{[A]_t^m [B]_t^n}$$

Enthalpy change for gas-phase reaction change...

$$\Delta_r H = \sum E_{\text{bonds broken}} - \sum E_{\text{bonds formed}}$$

Standard state enthalpy change...

$$\Delta_r H^\circ = H_{\text{products}}^\circ - H_{\text{reactants}}^\circ$$

Relation between $\Delta_r H^\circ$ and $\Delta_f H^\circ$...

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

Standard entropy change...

$$\Delta_r S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

Free energy based on enthalpy, entropy, and temperature...

$$\Delta_r G^\circ = \Delta_r H - T \Delta_r S^\circ$$

Free energy...

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

Relationship between free energy and the equilibrium constant...

$$\Delta_r G^\circ = -RT \ln K^\circ$$

Relating reaction rate and equilibrium constant...

$$K = \frac{k_{\text{forward}}}{k_{\text{reverse}}} = \frac{Ae^{-\frac{E_a(\text{forward})}{RT}}}{Ae^{-\frac{E_a(\text{reverse})}{RT}}} = e^{-\frac{[E_a(\text{forward}) - E_a(\text{reverse})]}{RT}}$$

EXAM: Monday, November 4th

5:45PM – 7:00PM @ PSYCH 105

Arrhenius equation...

$$k = Ae^{-\frac{E_a}{RT}}$$

van't Hoff equation...

$$\ln K = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta_r S^\circ}{R}$$

Arrhenius slope equation...

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln A$$

ALL CHEMICAL/PHYSICAL CHANGES TEND TOWARDS EQUILIBRIUM

For a chemical reaction...

- ➔ Forwards and reverse reactions occur at the same rate, and the concentrations of products and reactants remain constant over time
- ➔ The same equilibrium concentrations can be achieved by starting with reactants only, products only, or a mixture of reactants and products, provided that the same total number of atoms of each kind is present

Equilibrium constant expressions...

<i>Equilibrium constant</i>	<u>K; ratio of equilibrium partial pressures (gas-phase) or equilibrium concentrations (liquid-phase) of products and reactants that has a specific value for a given reaction at a given temperature</u>
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Consider $mA + nB \rightleftharpoons xC + yD$

$$K = \frac{p_C^x p_D^y}{p_A^m p_B^n} \text{ (gas-phase)}$$

$$K = \frac{[C]^x [D]^y}{[A]^m [B]^n} \text{ (liquid-phase)}$$

<i>Homogenous equilibrium</i>	<u>all of the reactants and products are present in a single phase</u>
<i>Heterogenous equilibrium</i>	<u>all of the reactants and products are found in two or more phases</u>

Favored reactions...

<i>Product-favored reaction</i>	<u>a reaction that proceeds spontaneously in the forward direction when all concentrations (or partial pressures) have a value of 1M (or 1 bar)</u>
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- ➔ If $K > 1$, concentration of products are greater than concentration of reactants
- ➔ The reaction is product favored at equilibrium

<i>Reactant-favored reaction</i>	<u>a reaction that proceeds spontaneously in the reverse direction when all concentrations (or partial pressures) have a value of 1M (or 1 bar)</u>
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- ➔ If $K < 1$, concentration of reactants are greater than concentration of products
- ➔ The reaction is reactant favored at equilibrium

MAKING PREDICTIONS ABOUT DIRECTION OF CHANGE

Reaction direction...

<i>Spontaneous</i>	<u>reactants change to products (spontaneous in the forward direction)</u>
<i>Not spontaneous</i>	<u>products change to reactants (spontaneous in the reverse direction)</u>
<i>Standard state</i>	<u>commonly accepted set of conditions used as a reference point (1 bar, 1M)</u>
<i>Product-favored</i>	<u>when all substances are at the standard-state conditions, reactants change to products</u>
<i>Reactant-favored</i>	<u>if products change to reactants under standard-state conditions</u>

Reaction quotient...

Consider $mA + nB \rightleftharpoons xC + yD$

$$Q = \frac{[C]_t^x [D]_t^y}{[A]_t^m [B]_t^n}$$

- ➔ If $Q = K$, the system is at equilibrium
- ➔ If $Q > K$, more reactants will be produced
- ➔ If $Q < K$, more products will be produced

Change in concentration...

<i>Le Chatelier's principle</i>	<u>when a chemical system is at equilibrium and conditions are changed so that the reaction is no longer at equilibrium, the chemical system reacts to achieve the new equilibrium concentrations or partial pressures in a way that partially counteracts the change in conditions</u>
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- ➔ "Add away, take towards"
- ➔ Increases volume, towards higher moles
- ➔ Decreases volume, towards less moles

ENERGY FLOWS ARE LINKED TO CHEMICAL CHANGE

Chemical reaction enthalpy...

→ Enthalpy change for gas-phase reaction change...

$$\Delta_r H = \sum E_{\text{bonds broken}} - \sum E_{\text{bonds formed}}$$

→ Rules to predict whether a chemical reaction releases energy

- If there are more product molecules than reactant molecules and the bonds have the same strength, the reaction is likely exothermic
- If there are stronger bonds in the product molecules than in the reactant molecules and $n_{\text{bonds}}(\text{reactants}) = n_{\text{bonds}}(\text{products})$, the reaction is likely exothermic

Standard-state reaction enthalpy change...

<i>Thermochemical expression</i>	<u>balanced chemical equation together with value of $\Delta_r H^\circ$ and temperature</u>
<i>Standard-state reaction enthalpy change</i>	<u>$\Delta_r H^\circ$; standard state enthalpy of pure, unmixed products minus the standard state enthalpy of pure, unmixed reactants'</u>

$$\Delta_r H^\circ = H_{\text{products}}^\circ - H_{\text{reactants}}^\circ$$

→ Conventions for thermochemical expressions

- $\Delta_r H^\circ \propto$ coefficients of chemical expression
- $\Delta_r H^\circ$ depends on the physical state of reactants and products (must include state in expression)
- $\Delta_r H^\circ < 0 \Rightarrow$ exothermic
- $\Delta_r H^\circ > 0 \Rightarrow$ endothermic
- If the sign of $\Delta_r H^\circ$ is changed, the direction of the reaction is reversed (and vice versa)

<i>Hess's law</i>	<u>if a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy change of the various steps</u>
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Standard formation enthalpy...

<i>Standard formation enthalpy</i>	<u>$\Delta_f H^\circ$; the enthalpy change for a reaction in which exactly one mole of a pure substance in a specified states formed from free elements in their most stable states under standard state conditions</u>
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→ Also called standard heat formation

→ Relation between $\Delta_r H^\circ$ and $\Delta_f H^\circ$...

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

WHY CHEMICAL/PHYSICAL CHANGES OCCUR

Entropy and microstates...

→ Entropy change,.

$$\Delta S = \frac{q_{rev}}{T}$$

where q_{rev} is the heat transfer of energy for a reversible process

Reversible process	<u>a theoretical process that takes place such that its direction can be changed by an infinitesimally small change in some condition</u>
Microstate	<u>specific configuration of the energies of a system</u>

$$S = k_B \ln W$$

$$k_B = 1.38 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$$

$$\Delta S = k_B \ln \left(\frac{W_f}{W_i} \right)$$

Entropy of substance-phases...

$$S_{gas} > S_{liquid} > S_{solid}$$

Standard entropy...

Third law of thermodynamics	<u>entropy of a pure, perfect crystalline structure at 0K is zero</u>
Standard entropy	<u>S°; absolute entropies per mole of a substance of pressure at 1 bar</u>

Standard entropy change...

$$\Delta_r S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

Second law of thermodynamics...

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

→ Possibilities for heat transfer process

- Object at different temperatures transfer energy from higher temperatures to lower temperatures

$$\Delta S_{sys} = \frac{-q_{rev}}{T_{sys}} \text{ and } \Delta S_{surr} = \frac{q_{rev}}{T_{surr}}$$

- Heat *never* transfers from low to high temperatures

Second law of thermodynamics	<u>all changes that take place on their own accord (are spontaneous) leading to an increase in entropy of the universe</u>
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- $\Delta S_{univ} > 0$: spontaneous (on its own accord)
- $\Delta S_{univ} < 0$: not spontaneous (reverse reaction occurs)
- $\Delta S_{univ} = 0$: system is at equilibrium

GIBBS FREE ENERGY

Relating enthalpy, entropy, and free energy...

$$G_{sys} = H_{sys} - TS_{sys}$$

- ➔ If $\Delta S_{univ} > 0, \Delta G_{sys} < 0 \Rightarrow$ spontaneous
- ➔ If $\Delta S_{univ} < 0, \Delta G_{sys} > 0 \Rightarrow$ not spontaneous
- ➔ If $\Delta S_{univ} = 0, \Delta G_{sys} = 0 \Rightarrow$ equilibrium

$$\Delta_r G^\circ = \Delta_r H - T\Delta_r S^\circ$$

Given $mA + nB \rightleftharpoons xC + yD...$

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants}) = [x\Delta_f G^\circ(C) + y\Delta_f G^\circ(D)] - [m\Delta_f G^\circ(A) + n\Delta_f G^\circ(B)]$$

Relating standard free energy and standard equilibrium constant....

$$\Delta_r G^\circ = -RT \ln K^\circ$$

$$K^\circ = e^{-\frac{\Delta_r G^\circ}{RT}}$$

- ➔ If $K^\circ > 0, \Delta_r G^\circ < 0 \Rightarrow$ product favored at equilibrium
- ➔ If $K^\circ < 0, \Delta_r G^\circ > 0 \Rightarrow$ reactant favored at equilibrium
- ➔ If $K^\circ = 0, \Delta_r G^\circ = 0 \Rightarrow$ product and reactant are equally abundant at equilibrium

SUBMICROSCOPIC COLLISIONS

Reaction energy diagrams...

<i>Reaction energy diagrams</i>	<u>diagram that shows energy as a function of reaction progress</u>
<i>Transition state</i>	<u>maximum on the reaction energy diagram</u>
<i>Transition-state structure</i>	<u>structure that corresponds to a transition state</u>
<i>Activation energy</i>	<u>difference in energy between the transition state and reactants</u>

Arrhenius equation...

$$k = Ae^{-\frac{E_a}{RT}}$$

<i>Steric factor</i>	<u>fraction of collisions energetic enough to react that actually results in a reaction</u>
<i>Frequency factor</i>	<u>A; depends on the rate at which collisions occur and the fraction of collisions that have the correct orientation (steric factor)</u>

Reaction rate...

<i>Rate of chemical reaction</i>	<u>change in concentration of a reactant or a product per unit of time</u>
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$$\text{rate} = k[\text{reactant A}]^m[\text{reactant B}]^n = k \prod [\text{reactant N}]^i$$

<i>Rate constant</i>	<u>a proportionality constant interdependent of a reactant concentrations is specific to a particular version at a particular temperature</u>
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➔ More factors to determine value of K...

- To react molecules, they must come close enough to exchange energy and possibly even form/break bonds; and when $c = 1M$: $k \propto \frac{\# \text{ of collisions}}{\text{time}}$
- For a reaction to occur, there must be sufficient energy to allow electrons to be rearranged; ↓ energy requirement, ↓ E_a , ↑ k
- Reacting molecules must collide in an orientation that allows a reaction to proceed; steric factor

CHEMICAL/PHYSICAL CHANGE IS DEPENDENT ON TEMPERATURE

Temperature dependence of Gibbs free energy...

→ Recall $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$

	$\Delta_r H^\circ > 0$ (endothermic)	$\Delta_r H^\circ < 0$ (exothermic)
$\Delta_r S^\circ > 0$ (system entropy increase)	$\Delta_r G^\circ > 0$ at low temperatures $\Delta_r G^\circ < 0$ at high temperatures Product-favored at high temperatures	$\Delta_r G^\circ < 0$ at low temperatures $\Delta_r G^\circ < 0$ at high temperatures Product-favored at all temperatures
$\Delta_r S^\circ < 0$ (system entropy decrease)	$\Delta_r G^\circ > 0$ at low temperatures $\Delta_r G^\circ > 0$ at high temperatures Reactant-favored at all temperatures	$\Delta_r G^\circ < 0$ at low temperatures $\Delta_r G^\circ > 0$ at high temperatures Product-favored at low temperatures

Effects of temperature on equilibrium...

→ Recall $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$, $\Delta_r G^\circ = -RT \ln K^\circ$

→ We can rearrange to get:

$$\ln K^\circ = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta_r S^\circ}{R}$$

→ Which takes the form of $y = mx + b$: the slope m is represented by $-\frac{\Delta_r H^\circ}{R}$

Application of Le Chatelier's principle to change in temperature...

→ $\Delta T > 0$, shifts the reaction in the endothermic direction (direction with $\Delta_r H^\circ > 0$)

→ $\Delta T < 0$, shifts the reaction in the exothermic direction (direction with $\Delta_r H^\circ < 0$)

→ Different concentrations the new equilibrium system corresponds to a different value for K

→ The larger the magnitude $\Delta_r H^\circ$, the larger the shift, and greater the ΔK

Relating activation energy, concentration, and reaction rate...

→ Recall Arrhenius equation, $k = Ae^{-\frac{E_a}{RT}}$

→ We can rearrange to get:

$$\ln k = \left(-\frac{E_a}{R} \right) \left(\frac{1}{T} \right) + \ln A$$

→ Which takes the form of $y = mx + b$: the slope m is represented by $-\frac{E_a}{R}$

Summary...

Enthalpy	Entropy	Description of q	Directionality
$\Delta_r H^\circ > 0$	$\Delta_r S^\circ < 0$	Endothermic	Towards reactants $\Delta_r G^\circ > 0$ at any temp T
$\Delta_r H^\circ < 0$	$\Delta_r S^\circ > 0$	Exothermic	Towards products $\Delta_r G^\circ < 0$ at any temp T
$\Delta_r H^\circ > 0$	$\Delta_r S^\circ > 0$	Endothermic	Towards products when $T > \frac{\Delta_r H^\circ}{\Delta_r S^\circ}$
$\Delta_r H^\circ < 0$	$\Delta_r S^\circ < 0$	Exothermic	Towards products when $T < \frac{\Delta_r H^\circ}{\Delta_r S^\circ}$

$\Delta_r H^\circ$	$\Delta_r S^\circ$	As T increases, $\Delta_r G^\circ$ becomes...	K prediction using $\Delta_r G^\circ$: $K...$	As T increases, $K...$
–	+	more negative	increases	decreases
–	–	more positive	decreases	decreases
+	–	more positive	decreases	increases
+	+	more negative	increases	increases

➔ NEVER use $\Delta_r G^\circ$ to reason about how T affects K

CONTROLLING EQUILIBIRUM COMPOSITION

Kinetic metastability...

<i>Thermodynamically stable</i>	when a reaction favors products at equilibrium ($\Delta_r G^\circ > 0$) (in discussion about the products)
<i>Kinetically metastable</i>	when a product favored reaction proceeds so slowly that it is considered to be non-occurring (in discussion about the reactants)

Competing reactions...

<i>Kinetic control</i>	where the product mixture is determined by reaction rates
<i>Thermodynamic control</i>	all reactions occur fast enough so that equilibrium can be achieved

Application of work to fuels...

→ Fuels require work

<i>Work</i>	a process that transfers kinetic energy to/from a macroscopic object
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$$w = -\Delta_r G$$

→ The $-\Delta_r G$ is the maximum value that can be done when a spontaneous process occurs