

AP Chemistry  
Exam Review

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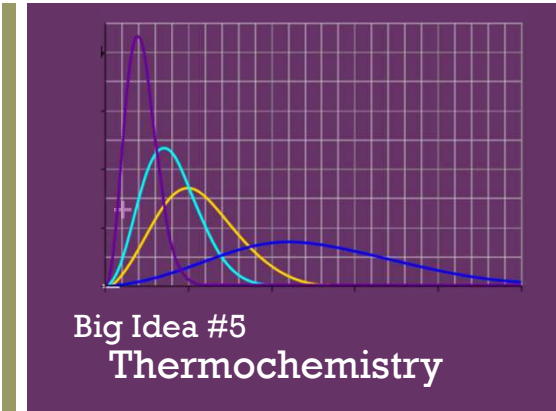
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Big Idea #5  
Thermochemistry

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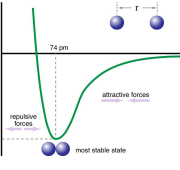
### + Bond Energy, Length & Strength

- Bond strength is determined by the distance between the atoms in a molecule and bond order. Multiple bonds shorten the distance & increase the force of attraction between atoms in a molecule.
- Bond Energy is **ENDOTHERMIC** –the energy needed to break the bond.

Bond	Length (pm)	Energy (kJ/mol)
C - C	154	346
C=C	134	612
C≡C	120	835
C - N	147	305
C=N	132	615
C≡N	116	887
C - O	143	358
C=O	120	799
C≡O	113	1072
N - N	145	180
N=N	125	418
N≡N	110	942

**3 Factors**

- Size:** H-Cl is smaller than H-Br
- Polarity:** HCl is more polar than H-C
- Bond order (length):** C=C involves more e<sup>-</sup> is shorter than C-C.



potential energy

74 pm

attractive forces

repulsive forces

-436 kJ/mol

most stable state

Lowest PE = Bond Energy

Source

Video

LO: 5.1 The student is able to create or use graphical representations in order to connect the dependence of potential energy to the distance between atoms and factors, such as bond order and polarity, which influence the interaction strength.

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### + Maxwell-Boltzmann Distributions

Source  
Video

- Temperature is a measure of the average Kinetic Energy of a sample of substance.
- Particles with larger mass will have a lower velocity but the same Average KE at the same Temperature.
- Kinetic Energy is directly proportional to the temperature of particles in a substance. (if you double the Kelvin Temp you double the KE)
- The M-B Distribution shows that the distribution of KE becomes greater at higher temperature.
- The areas under the curve are equal and therefore the number of molecules is constant
- Increasing Temperature (KE) increases the number of particles with the Activation Energy necessary to react.
- Activation Energy is not changed with temperature but may be changed with a catalyst.

LO 5.2: The student is able to relate Temp to motions of particles in particulate representations including velocity, and/ or via KE and distributions of KE of the particles.

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### + Thermodynamic vocabulary

Source  
Video

- Universe:** The sum of the system and surroundings
- System:** The species we want to study
- Surroundings:** the environment outside the system
- Endothermic:** Heat flows to the system from the surroundings (surroundings temperature drops-i.e. beaker feels cold)
- Exothermic:** Heat flows from the system to the surroundings. (surroundings temperature rises-i.e. beaker feels hot)

LO 5.3: The student can generate explanations or make predictions about the transfer of thermal energy between systems based on this transfer being due to a kinetic energy transfer between systems arising from molecular collisions.

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### + Heat Transfer

Source  
Video

- Kinetic energy transferred between particles of varying temperature is heat energy.
- Heat flows from particles of higher energy (hot) to those of lower energy (cold) when particles collide.
- When the temperature of both particles are equal the substances are in thermal equilibrium.
- Not all particles will absorb or release the same amount of heat per gram.
- Specific Heat Capacity is a measure of the amount of heat energy in Joules that is absorbed to raise the temperature of 1 gram of a substance by 1 degree Kelvin.
- Heat transfer can be measured  $q = mc_p \Delta T$

LO 5.3: The student can generate explanations or make predictions about the transfer of thermal energy between systems based on this transfer being due to a kinetic energy transfer between systems arising from molecular collisions.

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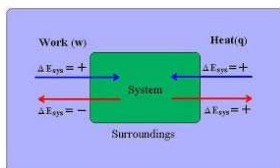
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## + Conservation of Energy

Source

- 1<sup>st</sup> Law of Thermodynamics: Energy is conserved
- Temperature is a measure of the average Kinetic energy of particles in a substance
- Energy can be transferred as Work or Heat
- $\Delta E = q + w$
- Work =  $-P\Delta V$  (this is the work a gas does on the surroundings i.e the volume expanding a piston) a gas does no work in a vacuum.

Video



LO 5.4: The student is able to use conservation of energy to relate the magnitude of the energy changes occurring in two or more interacting systems, including identification of the systems, the type (heat vs. work), or the direction of the energy flow.

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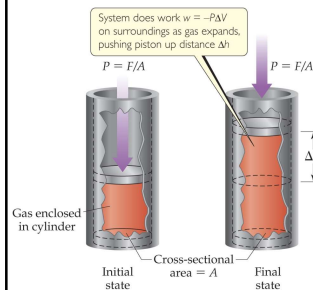
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## + Conservation of Energy

Source



- Expansion/Compression of a gas
- Volume increases, work is done by the gas
- Volume decreases, work is done on the gas

Video

LO 5.4: The student is able to use conservation of energy to relate the magnitude of the energy changes occurring in two or more interacting systems, including identification of the systems, the type (heat vs. work), or the direction of the energy flow.

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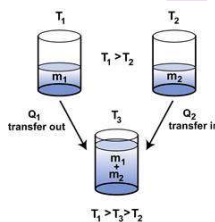
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## + Conservation of Energy when Mixing

Source

- Energy is transferred between systems in contact with one another
- Energy lost by one system is gained by the other so that total energy is always conserved.
- $-Q$  lost by system =  $+Q$  gained by surroundings
- For example :
  - When room temperature water  $T_1$  (system) is mixed with cold water  $T_2$  (surroundings), the final temperature  $T_3$  will be in-between.
- $Q_1 + Q_2 = 0$  and energy is conserved

Video



LO 5.5: The student is able to use conservation of energy to relate the magnitudes of the energy changes when two non reacting substances are mixed or brought into contact with one another.

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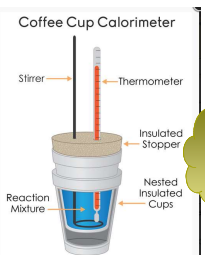
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**Calorimetry:** an experimental technique used to determine the heat transferred in a chemical system. System can be a chemical reaction or physical process.

- Can use Calorimetry to solve for Heat Capacity of a calorimeter ( $C$ ), specific heat of a substance, ( $c$ ), and  $\Delta H_{vap}$ ,  $\Delta H_{fus}$ ,  $\Delta H_{rxn}$ .
- The data handling and math:
  - Law of Conservation of Energy:  $Q_{system} + Q_{surroundings} = 0$
  - $Q_{system} = -Q_{surroundings}$  where System = reaction, Surroundings = calorimeter
  - SO:  $Q_{rxn} = -Q_{calorimeter}$
  - Heat Transfer due to Temperature Change in the Calorimeter:
    - $Q = C\Delta T$ , or  $Q = mc\Delta T$  where  $Q$  in J,  $C$  in J/K,  $m$  in g,  $c$  in J/g-K,  $\Delta T$  in K
  - $Q_{rxn} = -Q_{calorimeter} = -C\Delta T$  if the calorimeter Heat Capacity is known, or can be determined.
  - $Q_{rxn} = -Q_{calorimeter} = -mc\Delta T$  for reactions in solution.
- When calculating  $\Delta H$ , must take into account the mass of reactant that caused  $Q_{rxn}$ .



**Figure 7-10. Coffee Cup Calorimeter**  
When a chemical reaction occurs in the coffee cup, the heat generated by the reaction will be absorbed by the water in the cup. Because Styrofoam is a good insulator, nearly all the thermal energy from the reaction will stay in the cup and not be lost to the surroundings during the experiment. (Unit 7, Section 7) © Science Media Group

**Source**  
[Video](#)

**Example problem in video**

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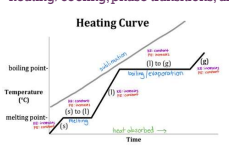
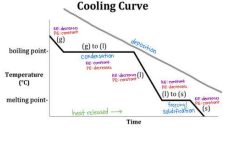
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LO 5.5: The student is able to use conservation of energy to relate the magnitudes of the energy changes when two non-reacting substances are brought into contact with one another.

Chemical Systems undergo 3 main processes that change their energy: heating/cooling, phase transitions, and chemical reactions.

- Heat Transfer due to Temperature Change: (KJ)**  
 $Q = mc\Delta T$   
 $m = \text{mass (g)}$ ,  $c = \text{specific heat capacity (J/g}^\circ\text{C)}$ ,  $\Delta T = \text{Temp. change in } ^\circ\text{C}$   
 $Q$  is + for Heating, - for cooling
- Heat Transfer due to Phase Change: (kJ/mol)**  
 $Q = \Delta H_{\text{phase change}}$   
 $Q$  phase change = + for  $\Delta H_{\text{fusion}}$ ,  $\Delta H_{\text{vaporizing}}$ ,  $\Delta H_{\text{subliming}}$ , - for  $\Delta H_{\text{freezing}}$ ,  $\Delta H_{\text{condensing}}$ ,  $\Delta H_{\text{deposition}}$
- $Q$  for a chemical reaction at constant pressure =  $\Delta H_{rxn}$**   
When calculating  $\Delta H_{rxn}$  from  $Q$ , remember  $\Delta H_{rxn}$  must agree with the stoichiometric coefficients in the reaction. Units of  $\Delta H_{rxn}$  are kJ/mol rxn.
- When a gas expands or contracts in a chemical reaction, energy is transferred in the form of Pressure-Volume work.**  $W = -P\Delta V$  (-atm)  
Gas Expands – Does work on surroundings (system loses energy)  
Gas Contracts – Work done on the gas (system gains energy)  
No change in volume, no work done.

**Source**  
[Video](#)

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LO 5.6: The student is able to use calculations or estimations to relate energy changes associated with heating/cooling a substance to the heat capacity, relate the energy changes associated with a phase transition to the enthalpy of fusion/vaporization, relate energy changes associated with a chemical reaction to the enthalpy of the reaction, and relate the energy changes to PΔV work.

**Calorimetry:** an experimental technique used to determine the heat transferred in a chemical system. System can be a chemical reaction or physical process.

**Question:**  
A student is using a calorimeter made from a polystyrene cup and a thermometer to determine the specific heat capacity of an unknown solid. The cup was weighed, then filled with 100mL of water. After the water reached equilibrium with the room the temperature was measured at 25.0°C. A piece of the unknown metal was found to

**Answer:**  
The correct answer is "b", the calculated value would be too small because of the heat lost to the surroundings. As the temperature of the water increases energy will be lost to the cooler surroundings. Having a top on the cup will minimize that loss, with out the cup the measured temperature will be lower than it should be, giving a lower value for the specific heat capacity.

- The calculated value would be too small because of the heat absorbed from the surroundings.
- The calculated value would not be changed.

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**Source**  
[Video](#)

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LO 5.7 The student is able to design and/or interpret the results of an experiment in which calorimetry is used to determine the change in enthalpy of a chemical process. (heating/cooling, phase transition, or chemical reaction) at constant pressure.

+ The net energy change during a reaction is the sum of the energy required to break the reactant bonds and the energy released in forming the product bonds. The net energy change may be positive for endothermic reactions where energy is required, or negative for exothermic reactions where energy is released.

Any bond that can be formed can be broken. These processes are in opposition; their enthalpy changes are equal in magnitude, opposite sign)

- >  $\Delta H$  bonds breaking  $\rightarrow$  ENDOTHERMIC (+)
- >  $\Delta H$  bonds forming  $\rightarrow$  EXOTHERMIC (-)
- > To find  $\Delta H_{rxn}$ , apply Hess's Law:
- >  $\Delta H_{rxn} = \Sigma \Delta H$  bonds breaking (+) +  $\Sigma \Delta H$  bonds forming (-)

**To calculate or estimate  $\Delta H_{rxn}$  from Bond Energy:**

1. Draw the Lewis Structure. Don't forget about double and triple bonds!
2. Add up  $\Delta H$  bonds breaking. It's + (kJ)
3. Add up  $\Delta H$  bonds forming. It's - (kJ).
4. Add the two terms. Units are kJ/mol rxn.

**To calculate  $\Delta H^\circ_{rxn}$  from a table of standard enthalpies of formation:**  
 $\Delta H^\circ_{rxn} = \Sigma \Delta H^\circ_f \text{ products} - \Sigma \Delta H^\circ_f \text{ reactants}$

**LO 5.8: The student is able to draw qualitative and quantitative connections between the reaction enthalpy and the energies involved in the breaking and formation of chemical bonds.**

Source

Video

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+ Electrostatic forces exist between molecules as well as between atoms or ions, and breaking these intermolecular interactions requires energy.

The **Stronger the IMF** the more energy required to break it, the **Higher the Boiling Point**, the **Lower the Vapor Pressure**.

**Intermolecular Forces Listed from weakest to strongest.** Thus the boiling points and vapor pressure of molecular substances can be ordered based on IMF strength:

Weaker IMF,  
Lower Boiling,  
Higher Vapor  
Pressure

1. **Dispersion (Induced Dipole- Induced Dipole):** Caused by distortion of electron cloud. The larger the electron cloud, and the more surface area, the more polarizable the cloud, the stronger the dispersion force. *Thus the boiling point trend in halogens is  $I_2 > Br_2 > Cl_2 > F_2$  and *n*-butane (30.2 °C) has a higher boiling point than isobutane (-11 °C). All substances have dispersion forces, as all electron clouds distort. Nonpolar molecules and atoms have only dispersion forces, as they have no permanent dipoles.*
2. **Dipole- Induced Dipole:** Occurs between a polar molecule (HCl) and a nonpolar molecule. (Cl<sub>2</sub>) The nonpolar molecule's cloud distorts when affected by a dipole.
3. **Dipole-Dipole:** Occurs between 2 polar molecules. (HCl-HCl)
4. **Hydrogen Bond:** An extreme case of Dipole - Dipole. Occurs between molecules containing a H covalently bonded to F, O, or N. The "bond" occurs between the lone pair of F, O, or N, and the H which is attached to one of those elements.

Stronger IMF,  
Higher Boiling,  
Lower Vapor  
Pressure

**LO 5.9: Make claims and/or predictions regarding relative magnitudes of the forces acting within collections of interacting molecules based on the distribution of electrons within the molecules and the types of intermolecular forces through which the molecules interact.**

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## Inter vs Intra Chemical vs. Physical

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Video

If you are asked to rank molecules in order of melting point, boiling point, viscosity, surface tension or vapour pressure ... what they are actually asking is for you to rank them by strength of intermolecular forces (either increasing or decreasing).

Here is my strategy for this:

1. Look for molecules with hydrogen bonding capability will have the strongest intermolecular forces.
2. Look for molecules with dipoles. These will have the next strongest intermolecular forces.
3. Larger molecules will have stronger London dispersion forces. These are the weakest intermolecular forces but will often be the deciding factor in multiple choice questions

**Strong IMF= High BP, High MP, High viscosity, high surface tension, low vapor pressure!**

**LO 5.10: The student can support the claim about whether a process is a chemical or physical change (or may be classified as both) based on whether the process involves changes in intramolecular versus intermolecular interactions.**

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# +IMF and Biological/Large Molecules

Source  
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Video

**Intermolecular forces in liquids and solids**  
Weak intermolecular forces (non-covalent interactions) act between molecules, causing them to be attracted to each other in varying degrees. The strength of these forces at a particular temperature determines whether a molecular substance is a gas, a liquid, or a solid at that temperature.

Non-covalent forces also contribute to the secondary, tertiary, or quaternary structure of macromolecules (mainly proteins and nucleic acids); maintain the stability of membranes, and play important roles in highly specific biological interactions (enzyme - substrate; antigen - antibody; signal molecules - receptor).

**Types of intermolecular forces:**

- hydrogen bonds
- dipole-dipole interactions
- dispersion forces (London forces).

Dipole-dipole and dispersion forces are sometimes referred to collectively as **van der Waals forces**.

This image shows the tertiary structure of a protein segment. Tertiary structure results from different interactions, or forces, between groups. Move the cursor to each force to the appropriate description on the protein. Then identify the major force controlling tertiary structure.

- hydrogen bond
- ionic bond
- hydrophobic interaction
- disulfide bond

continued

LO 5.11: The student is able to identify the noncovalent interactions within and between large molecules, and/or connect the shape and function of the large molecule to the presence and magnitude of these interactions.

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# + Entropy- Embrace the Chaos!

Source  
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Video

**Entropy Changes that result in a  $\Delta S$ :**

- Increasing moles
- Increasing temperature
- Increasing volume
- Solid to liquid to gas
- Forming more complicated molecules. (More moles of electrons)

More gas in product - Entropy ↑

Increasing entropy

$\Delta S > 0$   
 $\Delta S < 0$

LO 5.12: The student is able to use representations and models to predict the sign and relative magnitude of the entropy change associated with chemical or physical processes.

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# Predicting How Reactions Will Go

Video #1  
Video #2  
Source

$\Delta G = \Delta H - T\Delta S$  when will delta G < 0

$\Delta H$	$\Delta S$	Thermodynamic Favorability
-	+	spontaneous at all temperatures
+	-	non-spontaneous at all temperatures
-	-	spontaneous at low temperatures non-spontaneous at high temperatures
+	+	non-spontaneous at low temperatures spontaneous at high temperatures

**CAUTION**  
Entropy is typically given in J/K so you MUST convert to kJ!

$\Delta G$  (Gibbs Free Energy)

Free Energy Change (kJ)  $\Delta G = \Delta H - T\Delta S$  Entropy Change (kJ/K)

System temperature (K)

Enthalpy change (kJ)

If  $G < 0$ , i.e. negative, the reaction is thermodynamically favored (spontaneous.)

LO 5.13: The student is able to predict whether or not a physical or chemical process is thermodynamically favored by determination of (either quantitatively or qualitatively) the signs of both delta H° and delta S°, and calculation or estimation of delta G° when needed.

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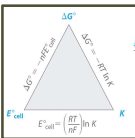
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## How can I calculate ΔG?



ΔG°	E°_cell	K	Direction of Reaction
< 0	> 0	> 1	spontaneous in forward direction
> 0	< 0	< 1	spontaneous in reverse direction
0	0	1	no net reaction: system at equilibrium

[Source](#)  
[Video](#)  
[Video](#)  
[Video](#)

### ΔG and K

- Standard free energy change is related to the thermodynamic equilibrium constant, K, at equilibrium.
  - IF a reaction is NOT at equilibrium, it is proceeding in some direction (forward or reverse) depending on Q, reaction quotient.
  - That means there exists energy to do work (make reaction proceed)
- $\Delta G = \Delta G^\circ + RT \ln Q$
- At equilibrium:
  - $\Delta G = 0$ , because there is no ability to do any more useful work
  - and  $Q = K$
- So we get:
  - $\Delta G^\circ = -RT \ln K$

$$\Delta G^\circ_{rxn} = \sum \Delta G^\circ_{(products)} - \sum \Delta G^\circ_{(reactants)}$$

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

$$\Delta G^\circ = -nFE$$

**LO 5.14:** Determine whether a chemical or physical process is thermodynamically favorable by calculating the change in standard Gibbs free energy

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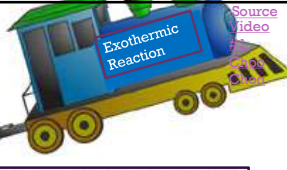
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## Coupling Reactions



[Source](#)  
[Video](#)

The sum of the free energy for these two reactions gives the overall  $\Delta G$  for this process ( $\Delta G = -16.7$  kJ/mol), which is very thermodynamically favorable. Another way in which reactions can be coupled is by breaking down a high energy compound with an enzyme, trapping that energy and using it to drive an endergonic reaction. You can think of energy as chemical currency used to conduct business in the cell. Taking this energy-as-money analogy a bit further, the coupling of the reactions is like what Robin Hood did in the Sherwood forest; stole from the rich and gave to the poor. Coupling reactions is a way to take the energy from the "rich" and bring it to the "poor" that really need it.

**LO 5.15:** Determine whether a chemical or physical process is thermodynamically favorable by calculating the change in standard Gibbs free energy

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## + Coupled Reactions and LeChatelier

$$A + B \rightleftharpoons C + D \rightleftharpoons D + E \rightleftharpoons F$$

Reactions can be coupled together if they share a common intermediate. In this example, the two reactions share the component "D".

Let us assume that the first reaction has a  $K_{eq}$  much less than 1, while the  $K_{eq}$  for the second reaction is much greater than 1.

**What will happen?** Most of the D formed by the first reaction (which is not much), will react with E (assuming E is present) and be removed from the system.

This will inhibit the C+D "back reaction", while the A+B "forward reaction" will continue.

More D will be produced, even though the reaction that produces it is unfavorable.

**LO: 5.16** The student can use LeChatelier's principle to make qualitative predictions for systems in which coupled reactions that share a common intermediate drive formation of a product.

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**K, Q, and ΔG**

There is a direct relationship between the equilibrium constant,  $K$ , and the free energy,  $\Delta G$ .

$\Delta G > 0$ ;  $K < 1$  "reactant favored"  
 $\Delta G < 0$ ;  $K > 1$  "product favored"  
 $\Delta G = 0$ ;  $K = 1$

$\Delta G = \Delta G^\circ + RT \ln(Q)$   
 At equilibrium,  $\Delta G = 0$ ;  $Q = K_{eq}$   
 $\Delta G^\circ = -RT \ln(K_{eq})$

I.C.  
co  
constant for the combined reaction.

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**Table 20.2 The Relationship Between  $\Delta G^\circ$  and  $K$  at 298 K**

$\Delta G^\circ$ (kJ)	$K$	Significance
200	$9 \times 10^{-36}$	Essentially no forward reaction; reverse reaction goes to completion
100	$3 \times 10^{-18}$	
50	$2 \times 10^{-9}$	
10	$2 \times 10^{-2}$	
1	$7 \times 10^{-1}$	Forward and reverse reactions proceed to same extent
0	1	
-1	1.5	
-10	$5 \times 10^1$	Forward reaction goes to completion; essentially no reverse reaction
-50	$6 \times 10^8$	
-100	$3 \times 10^{17}$	
-200	$1 \times 10^{35}$	

I.5.  
pro  
and  
produce large amounts of product for certain sets of initial conditions.

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