Big Idea #5
Thermochemistry
Bond Energy, Length & Strength

- Bond strength is determined by the distance between the atoms in a molecule and bond order. Multiple bonds (double, triple) shorten the distance & increase the force of attraction between atoms in a molecule.

- Bond Energy is always ENDOTHERMIC – the energy needed to break the bond.

<table>
<thead>
<tr>
<th>Single Bond Energies (kJ/mol of bonds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
</tr>
<tr>
<td>436</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Multiple Bond Energies (kJ/mol of bonds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C</td>
</tr>
<tr>
<td>602</td>
</tr>
<tr>
<td>C≡C</td>
</tr>
<tr>
<td>1072</td>
</tr>
<tr>
<td>N≡N</td>
</tr>
<tr>
<td>945</td>
</tr>
</tbody>
</table>

3 Factors
1) Size: H-Cl is smaller than H-Br

2) Polarity: HCl is more polar than H-C

3) Bond order (length) C=C involves more e- is shorter than C-C.

Lowest PE = Bond Energy

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.
LO 5.1 Practice FRQ
from 2005 B

1)

(c) The bond energy of the carbon-to-sulfur bond in $\text{CS}_2$ is $577 \text{ kJ mol}^{-1}$. Is the bond energy of the carbon-to-selenium bond in $\text{CSe}_2$ expected to be greater than, less than, or equal to this value? Justify your answer.
The bond energy of the carbon-to-sulfur bond in $\text{CS}_2$ is 577 kJ mol$^{-1}$. Is the bond energy of the carbon-to-selenium bond in $\text{CSe}_2$ expected to be greater than, less than, or equal to this value? Justify your answer.
Maxwell–Boltzmann Distributions

- 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.
(b) Consider the three gases in the tank at 327°C: CH₃OH(g), CO(g), and H₂(g).

(i) How do the average kinetic energies of the molecules of the gases compare? Explain.

(ii) Which gas has the highest average molecular speed? Explain.
(b) Consider the three gases in the tank at 327°C: CH₃OH(g), CO(g), and H₂(g).

(i) How do the average kinetic energies of the molecules of the gases compare? Explain.

The average kinetic energies are the same because all three gases are at the same temperature.

1 point is earned for the correct answer and explanation.

(ii) Which gas has the highest average molecular speed? Explain.

\[ KE = \frac{1}{2}mv^2 \], so at a given temperature the molecules with the lowest mass have the highest average speed. Therefore the molecules in H₂ gas have the highest average molecular speed.

1 point is earned for the correct answer and explanation.
Thermodynamic vocabulary

- **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.
3) LO 5.3 Practice FRQ from 2010

A student performs an experiment to determine the molar enthalpy of solution of urea, $\text{H}_2\text{NCONH}_2$. The student places 91.95 g of water at 25°C into a coffee cup calorimeter and immerses a thermometer in the water. After 50 s, the student adds 5.13 g of solid urea, also at 25°C, to the water and measures the temperature of the solution as the urea dissolves. A plot of the temperature data is shown in the graph below.

![Graph showing temperature vs. time](image)

(b) According to the data, is the dissolution of urea in water an endothermic process or an exothermic process? Justify your answer.
LO 5.3 Practice FRQ from 2010

3) A student performs an experiment to determine the molar enthalpy of solution of urea, $\text{H}_2\text{NCONH}_2$. The student places 91.95 g of water at 25°C into a coffee cup calorimeter and immerses a thermometer in the water. After 50 s, the student adds 5.13 g of solid urea, also at 25°C, to the water and measures the temperature of the solution as the urea dissolves. A plot of the temperature data is shown in the graph below.

(b) According to the data, is the dissolution of urea in water an endothermic process or an exothermic process? Justify your answer.

The process is endothermic. The decrease in temperature indicates that the process for the dissolution of urea in water requires energy. One point is earned for the correct choice with justification.
Heat Transfer

- 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.
LO 5.3 Practice FRQ continued from 2010

4)

(c) Assume that the specific heat capacity of the calorimeter is negligible and that the specific heat capacity of the solution of urea and water is 4.2 J g\(^{-1}\) °C\(^{-1}\) throughout the experiment.

(i) Calculate the heat of dissolution of the urea in joules.

Reveal Answer
(c) Assume that the specific heat capacity of the calorimeter is negligible and that the specific heat capacity of the solution of urea and water is 4.2 J g\(^{-1}\) °C\(^{-1}\) throughout the experiment.

(i) Calculate the heat of dissolution of the urea in joules.

Assuming that no heat energy is lost from the calorimeter and given that the calorimeter has a negligible heat capacity, the sum of the heat of dissolution, \(q_{\text{soln}}\) and the change in heat energy of the urea-water mixture must equal zero.

\[ q_{\text{soln}} + mc\Delta T = 0 \quad \Rightarrow \quad q_{\text{soln}} = -mc\Delta T \]

\[ m_{\text{soln}} = 5.13 \text{ g} + 91.95 \text{ g} = 97.08 \text{ g} \]

\[ q_{\text{soln}} = -(97.08 \text{ g})(4.2 \text{ J g}^{-1}\text{°C}^{-1})(-3.2^\circ \text{C}) = 1.3 \times 10^3 \text{ J} \]

One point is earned for the correct setup.

One point is earned for the correct numerical result for the heat of dissolution.
Conservation of Energy

- 1st Law of Thermodynamics: Energy is conserved
- 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.

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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Conservation of Energy when Mixing

- 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

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.
**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 \(\Delta H_{\text{vap}}, \Delta f_{\text{us}}, \Delta H_{\text{rxn}}\).
- The data handling and math:
  - **Law of Conservation of Energy:** \(Q_{\text{system}} + Q_{\text{surroundings}} = 0\)
  - \(Q_{\text{system}} = -Q_{\text{surroundings}}\) where System = reaction, Surroundings = calorimeter
  - **SO:** \(Q_{\text{rxn}} = -Q_{\text{calorimeter}}\)
  - 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
  - \(Q_{\text{rxn}} = -Q_{\text{calorimeter}} = -C\Delta T\) if the calorimeter Heat Capacity is Known, or can be determined.
  - \(Q_{\text{rxn}} = -Q_{\text{calorimeter}} = -mc\Delta T\) for reactions in solution.

- **When calculating \(\Delta H\), must take into account the mass of reactant that caused \(Q_{\text{rxn}}\).**

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.
A student investigates the enthalpy of solution, $\Delta H_{\text{soln}}$, for two alkali metal halides, LiCl and NaCl. In addition to the salts, the student has access to a calorimeter, a balance with a precision of $\pm 0.1$ g, and a thermometer with a precision of $\pm 0.1^\circ$C.

(a) To measure $\Delta H_{\text{soln}}$ for LiCl, the student adds 100.0 g of water initially at 15.0$^\circ$C to a calorimeter and adds 10.0 g of LiCl(s), stirring to dissolve. After the LiCl dissolves completely, the maximum temperature reached by the solution is 35.6$^\circ$C.

(i) Calculate the magnitude of the heat absorbed by the solution during the dissolution process, assuming that the specific heat capacity of the solution is 4.18 J/(g·$^\circ$C). Include units with your answer.
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\[
q = mc\Delta T = (110.0 \text{ g})(4.18 \text{ J/(g·°C)})(35.6^\circ \text{C} - 15.0^\circ \text{C})
\]

\[
= 9,470 \text{ J} = 9.47 \text{ kJ}
\]

1 point is earned for the correct setup.
1 point is earned for the correct answer with units.
Chemical Systems undergo 3 main processes that change their energy: heating/cooling, phase transitions, and chemical reactions.

1. **Heat Transfer due to Temperature Change: (kJ)**
   \[ Q = mc\Delta T \]
   - \( m \) = mass (g), \( c \) = specific heat capacity (J/g\(^\circ\)C), \( \Delta T \) = Temp. change in °C
   - \( Q \) is + for Heating, - for cooling

2. **Heat Transfer due to Phase Change: (kJ/mol)**
   \[ Q = \Delta H \text{ phase change} \]
   - \( Q \) phase change = + for \( \Delta H \) fusion, \( \Delta H \) vaporizing, \( \Delta H \) subliming, - for \( \Delta H \) freezing, \( \Delta H \) condensing, \( \Delta H \) deposition

3. **Q for a chemical reaction at constant pressure = \( \Delta H \text{ rxn} \)**
   When calculating \( \Delta H \text{ rxn} \) from \( Q \), remember \( \Delta H \text{ rxn} \) must agree with the stoichiometric coefficients in the reaction.
   - Units of \( \Delta H \text{ rxn} \) are kJ/mol rxn.

4. **When a gas expands or contracts in a chemical reaction, energy is transferred in the form of Pressure-Volume work.**
   \[ W = -P\Delta V \text{ (l-atm)} \]
   - 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.

**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 weigh 50.0 g, the solid was heated to 100.0°C. After the solid was placed in the water the temperature of the water reached a maximum temperature of 40.0°C. During the experiment the student failed to put a top on the cup, how would this have affected the calculated value for the specific heat capacity of the unknown solid.

a. The calculated value would be too large because of the heat absorbed from the surroundings.
b. The calculated value would be too small because of the heat lost to the surroundings.
c. The calculated value would be too large because of the heat lost to the surroundings.
d. The calculated value would be too small because of the heat absorbed from the surroundings.
e. The calculated value would not be changed.

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

Question:
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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.

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

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)

- ΔH bonds breaking → ENDOThERMIC (+)
- ΔH bonds forming → EXOTHERMIC (-)

To find ΔH_{rxn}, apply Hess’s Law:

ΔH_{rxn} = ΣΔH bonds breaking (+) + Σ ΔH bonds forming (-)

To calculate or estimate ΔH_{rxn} from Bond Energy:
1. Draw the Lewis Structure. Don’t forget about double and triple bonds!
2. Add up ΔH bonds breaking. It’s + (kJ)
3. Add up ΔH bonds forming. It’s - (kJ).
4. Add the two terms. Units are kJ/mol rxn.

To calculate ΔH°_{rxn} from a table of standard enthalpies of formation:

ΔH°_{rxn} = ΣΔH°_f products - ΣΔH°_f reactants

If a reaction is EXOTHERMIC, there is a **net release in energy**, since weaker bonds break and stronger bonds form. Product has higher kinetic energy and lower potential energy than reactant.

If a reaction is ENDOTHERMIC, there is a **net absorption of energy**, since stronger bonds break, and weaker bonds form. Product has lower kinetic energy, and higher potential energy than reactant.

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.
LO 5.8 Practice FRQ from 2003

Answer the following questions that relate to the chemistry of nitrogen.

(a) Two nitrogen atoms combine to form a nitrogen molecule, as represented by the following equation.

\[ 2 \text{N}(g) \rightarrow \text{N}_2(g) \]

Using the table of average bond energies below, determine the enthalpy change, \( \Delta H \), for the reaction.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Average Bond Energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>N – N</td>
<td>160</td>
</tr>
<tr>
<td>N = N</td>
<td>420</td>
</tr>
<tr>
<td>N = N</td>
<td>950</td>
</tr>
</tbody>
</table>
LO 5.8 Practice FRQ from 2003

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<td>160</td>
</tr>
<tr>
<td>N = N</td>
<td>420</td>
</tr>
<tr>
<td>N ≡ N</td>
<td>950</td>
</tr>
</tbody>
</table>

\[ \Delta H = -950 \text{ kJ} \]

The reaction is exothermic because the chemical equation shows the formation of the N ≡ N bond.

1 point for correct sign
1 point for magnitude
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:

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 I₂ > Br₂ > Cl₂ > F₂ 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. (Cl₂) 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.

**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.
(b) Structures of the dimethyl ether molecule and the ethanol molecule are shown below. The normal boiling point of dimethyl ether is 250 K, whereas the normal boiling point of ethanol is 351 K. Account for the difference in boiling points. You must discuss both of the substances in your answer.
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The intermolecular forces of attraction among molecules of dimethyl ether consist of London (dispersion) forces and weak dipole-dipole interactions. In addition to London forces and dipole-dipole interactions that are comparable in strength to those in dimethyl ether, ethanol can form hydrogen bonds between the \( \text{H} \) of one molecule and the \( \text{O} \) of a nearby ethanol molecule. Hydrogen bonds are particularly strong intermolecular forces, so they require more energy to overcome during the boiling process. As a result, a higher temperature is needed to boil ethanol than is needed to boil dimethyl ether.

One point is earned for recognizing that ethanol molecules can form intermolecular hydrogen bonds, whereas dimethyl ether molecules do not form intermolecular hydrogen bonds.

One point is earned for recognizing that, compared to the energy required to overcome the weaker intermolecular forces in liquid dimethyl ether, more energy is required to overcome the stronger hydrogen bonds in liquid ethanol, leading to a higher boiling point.
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.

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 Practice FRQ from 2013

Answer the following questions using principles of molecular structure and intermolecular forces.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Empirical Formula</th>
<th>Solubility in Water</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₂H₆O</td>
<td>Slightly soluble</td>
<td>−24</td>
</tr>
<tr>
<td>2</td>
<td>C₂H₆O</td>
<td>Soluble</td>
<td>78</td>
</tr>
</tbody>
</table>

Compounds 1 and 2 in the data table above have the same empirical formula, but they have different physical properties. (a) The skeletal structure for one of the two compounds is shown below in Box X.

(i) Complete the Lewis electron-dot diagram of the molecule in Box X. Include any lone (nonbonding) pairs of electrons.

(ii) In Box Y above, draw the complete Lewis electron-dot diagram for the other compound, which is a structural isomer of the compound represented in Box X. Include any lone (nonbonding) pairs of electrons.
FRQ cont...

9) (b) On the basis of the complete Lewis electron-dot diagrams you drew in part (a) and the information in the data table above, identify which compound, 1 or 2, has the structure represented in Box X. Justify your answer in terms of the intermolecular forces present in each compound.

Use the information in the following table to answer parts (c) and (d).

<table>
<thead>
<tr>
<th>Name</th>
<th>Lewis Electron-Dot Diagram</th>
<th>Boiling Point (°C)</th>
<th>Vapor Pressure at 20°C (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloromethane</td>
<td>H :Cl :C :H</td>
<td>39.6</td>
<td>353</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>:Cl :Cl :Cl :Cl</td>
<td>76.7</td>
<td>89</td>
</tr>
</tbody>
</table>

(c) Dichloromethane has a greater solubility in water than carbon tetrachloride has. Account for this observation in terms of the intermolecular forces between each of the solutes and water.

(d) In terms of intermolecular forces, explain why dichloromethane has a higher vapor pressure than carbon tetrachloride.
Compound 2 is in Box X. Compound 2 (X) would have intermolecular hydrogen bonding. Compound 1 (Y) would have weaker dipole-dipole and London dispersion forces (LDFs). Because compound 2 has stronger intermolecular forces (IMFs) it has a higher boiling point. Also, compound 2 is capable of forming more hydrogen bonds with $\text{H}_2\text{O}$ than compound 1 is, causing the solubility difference noted in the table.

CH$_2$Cl$_2$ is polar, whereas CCl$_4$ is not. Therefore, CH$_2$Cl$_2$ interacts with H$_2$O via dipole-dipole forces, while CCl$_4$ only interacts with water via dipole-induced dipole forces or LDFs, which would be weaker. As a result, CH$_2$Cl$_2$ has a greater solubility.

Because CH$_2$Cl$_2$ has the higher vapor pressure, the combination of LDFs and dipole-dipole forces in CH$_2$Cl$_2$ must be weaker than the strong LDFs in CCl$_4$.
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.
Entropy - Embrace the Chaos!

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)

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.
10) \[ \text{CO}(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g) \]

The combustion of carbon monoxide is represented by the equation above.

(b) Determine the value of the standard entropy change, \( \Delta S_{\text{rxn}}^0 \), for the combustion of \( \text{CO}(g) \) at 298 K using the information in the following table.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( S_{298}^0 ) (J mol(^{-1}) K(^{-1}))</th>
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<tbody>
<tr>
<td>CO(g)</td>
<td>197.7</td>
</tr>
<tr>
<td>CO(_2)(g)</td>
<td>213.7</td>
</tr>
<tr>
<td>O(_2)(g)</td>
<td>205.1</td>
</tr>
</tbody>
</table>
10) LO 5.12 FRQ practice from 2006

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<tr>
<td>( \text{CO}_2(g) )</td>
<td>213.7</td>
</tr>
<tr>
<td>( \text{O}_2(g) )</td>
<td>205.1</td>
</tr>
</tbody>
</table>

\[ \Delta S_{\text{ran}}^0 = 213.7 \text{ J mol}^{-1} \text{ K}^{-1} - (197.7 \text{ J mol}^{-1} \text{ K}^{-1} + \frac{1}{2}(205.1 \text{ J mol}^{-1} \text{ K}^{-1})) \]
\[ = - 86.5 \text{ J mol}^{-1} \text{ K}^{-1} \]

One point is earned for taking one-half of \( S_{298}^0 \) for \( \text{O}_2(g) \).
One point is earned for the answer (with sign).
Predicting How Reactions Will Go

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 $\Delta H^\circ$ and $\Delta S^\circ$, and calculation or estimation of $\Delta G^\circ$ when needed.

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

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>Thermodynamic Favorability</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>+</td>
<td>spontaneous at all temperatures</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>non-spontaneous at all temperatures</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>spontaneous at low temperatures; non-spontaneous at high temperatures</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>spontaneous at high temperatures; non-spontaneous at low temperatures</td>
</tr>
</tbody>
</table>

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

$\Delta G$ (Gibbs Free Energy)

If $G < 0$, i.e. negative, the reaction is thermodynamically favored (spontaneous.)
How can I calculate $\Delta G$?

**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:
  - $\Delta G^\circ = -RT \ln K$

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

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

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

LO 5.14: Determine whether a chemical or physical process is thermodynamically favorable by calculating the change in standard Gibbs free energy
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 an $K_{eq}$ 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.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>$\Delta H^\circ_{298}$</th>
<th>$\Delta S^\circ_{298}$</th>
<th>$\Delta G^\circ_{298}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>C(s) + H₂O(g) $\rightleftharpoons$ CO(g) + H₂(g)</td>
<td>+131 kJ mol⁻¹</td>
<td>+134 J mol⁻¹ K⁻¹</td>
<td>+91 kJ mol⁻¹</td>
</tr>
<tr>
<td>Y</td>
<td>CO₂(g) + H₂(g) $\rightleftharpoons$ CO(g) + H₂O(g)</td>
<td>+41 kJ mol⁻¹</td>
<td>+42 J mol⁻¹ K⁻¹</td>
<td>+29 kJ mol⁻¹</td>
</tr>
<tr>
<td>Z</td>
<td>2 CO(g) $\rightleftharpoons$ C(s) + CO₂(g)</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>

(b) For reaction X, will the equilibrium constant, $K_p$, increase, decrease, or remain the same if the temperature rises above 298 K? Justify your answer.
LO 5.16 FRQ Practice from 2009

11)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>( \Delta H^\circ_{298} )</th>
<th>( \Delta S^\circ_{298} )</th>
<th>( \Delta G^\circ_{298} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>C(s) + H(_2)O(g) ⇋ CO(g) + H(_2)(g)</td>
<td>+131 kJ mol(^{-1})</td>
<td>+134 J mol(^{-1}) K(^{-1})</td>
<td>+91 kJ mol(^{-1})</td>
</tr>
<tr>
<td>Y</td>
<td>CO(_2)(g) + H(_2)(g) ⇋ CO(g) + H(_2)O(g)</td>
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<td>+42 J mol(^{-1}) K(^{-1})</td>
<td>+29 kJ mol(^{-1})</td>
</tr>
<tr>
<td>Z</td>
<td>2 CO(g) ⇋ C(s) + CO(_2)(g)</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>

(b) For reaction X, will the equilibrium constant, \( K_p \), increase, decrease, or remain the same if the temperature rises above 298 K? Justify your answer.

\( K_p \) will increase.

If the temperature is increased for an endothermic reaction (\( \Delta H^\circ_{298} = +131 \text{ kJ mol}^{-1} \)), then by Le Chatelier’s principle the reaction will shift toward products, thereby absorbing energy. With greater concentrations of products at equilibrium, the value of \( K_p \) will increase.

**OR**

Because \( \Delta G^\circ = -RT \ln K_p = \Delta H^\circ_{298} - T \Delta S^\circ_{298} \),

then \( \ln K_p = \frac{\Delta H^\circ_{298}}{RT} + \frac{\Delta S^\circ_{298}}{R} \).

An increase in \( T \) for a positive \( \Delta H^\circ_{298} \) results in an increase in \( \ln K_p \) and thus an increase in \( K_p \).
The student can make quantitative predictions for systems involving coupled reactions that share a common intermediate, based on the equilibrium constant for the combined reaction.

Manipulating $K_{eq}$

**Stepwise Equilibrium**

1. $N_2(g) + O_2(g) \rightarrow 2NO(g)$
   
   $K_{eq,1} = \frac{[NO]^2}{[N_2][O_2]}$

2. $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
   
   $K_{eq,2} = \frac{[NO_2]^2}{[NO]^2[O_2]}$

Determine the chemical equation for the overall process. What is the equilibrium constant for the overall process? How does it depend on the value of $K_{c_1}$ and $K_{c_2}$?

$$K_{eq} = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]} = K_{eq,1} \times K_{eq,2}$$

- A $\rightarrow$ B $\Delta G^{0}_1$
- B $\rightarrow$ C $\Delta G^{0}_2$

Sum: A $\rightarrow$ C $\Delta G^{0}_1 + \Delta G^{0}_2$

This principle of bioenergetics explains how a thermodynamically unfavorable (endergonic) reaction can be driven in the forward direction by coupling it to a highly exergonic reaction through a common intermediate.
Is it thermo, kinetics, or K?

THERMODYNAMICALLY FAVORABLE

Kinetics tells us how FAST a reaction will proceed. Equilibrium tells us how FAR a reaction proceeds. Thermodynamics tells us whether or not the reaction is FAVORABLE at a given temperature.

A reaction that is thermodynamically favorable will form more products at equilibrium BUT the reaction may be so SLOW that few products form in a reasonable amount of time.

L 5.18: Explain why a thermodynamically favored chemical reaction may not produce large amounts of product (based on consideration of both initial conditions and kinetic effects), or why a thermodynamically unfavored chemical reaction can produce large amounts of product for certain sets of initial conditions.
**ΔG° and the Equilibrium Constant**

The free energy at non-standard, non-equilibrium states is given by:

$$\Delta G = \Delta G^o + RT \ln(Q)$$

At equilibrium, $\Delta G = 0$ and $Q$ becomes “$K$”

$$\Delta G^o = -RT \ln(K)$$

Thermodynamically favorable (aka spontaneous) means a reaction is PRODUCT favored at a given temperature.

- $K > 1$, $\ln(K)$ is positive, $\Delta G^o$ is negative

**As $K$ decreases, $\Delta G^o$ becomes more positive**

---

L 5.18: Explain why a thermodynamically favored chemical reaction may not produce large amounts of product (based on consideration of both initial conditions and kinetic effects), or why a thermodynamically unfavored chemical reaction can produce large amounts of product for certain sets of initial conditions.
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Table 20.2 The Relationship Between $\Delta G^\circ$ and $K$ at 298 K

<table>
<thead>
<tr>
<th>$\Delta G^\circ$ (kJ)</th>
<th>$K$</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>$9 \times 10^{-36}$</td>
<td>Essentially no forward reaction; reverse reaction goes to completion</td>
</tr>
<tr>
<td>100</td>
<td>$3 \times 10^{-18}$</td>
<td>reverse reaction goes to completion</td>
</tr>
<tr>
<td>50</td>
<td>$2 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>$2 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>$7 \times 10^{-1}$</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>Forward and reverse reactions proceed to same extent</td>
</tr>
<tr>
<td>-1</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>-10</td>
<td>$5 \times 10^1$</td>
<td></td>
</tr>
<tr>
<td>-50</td>
<td>$6 \times 10^8$</td>
<td></td>
</tr>
<tr>
<td>-100</td>
<td>$3 \times 10^{17}$</td>
<td>Forward reaction goes to completion; essentially no reverse reaction</td>
</tr>
<tr>
<td>-200</td>
<td>$1 \times 10^{35}$</td>
<td></td>
</tr>
</tbody>
</table>
Is it thermo, kinetics, or $K$?

<table>
<thead>
<tr>
<th>Equilibrium constant</th>
<th>Description</th>
<th>Standard Gibbs Free Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K = 1$</td>
<td>Neither reactant nor product favored</td>
<td>$\Delta G^o = 0$</td>
</tr>
<tr>
<td>$K &gt; 1$</td>
<td>Product favored</td>
<td>$\Delta G^o &lt; 0$ (thermodynamically favorable)</td>
</tr>
<tr>
<td>$K &lt; 1$</td>
<td>Reactant favored</td>
<td>$\Delta G^o &gt; 0$ (thermodynamically unfavorable)</td>
</tr>
</tbody>
</table>

“Thermodynamically UNFAVORABLE” (aka non-spontaneous) reactions will run in reverse when set up with standard conditions (1M/1atm of ALL reactants and products) BUT can be made to proceed forward under different conditions.

produce large amounts of product (based on consideration of both initial conditions and kinetic effects), or why a thermodynamically unfavored chemical reaction can produce large amounts of product for certain sets of initial conditions.
Answer the following questions about the thermodynamics of the reactions represented below.

Reaction X: \( \frac{1}{2} \text{I}_2(s) + \frac{1}{2} \text{Cl}_2(g) \rightleftharpoons \text{ICl}(g) \)  \( \Delta H^\circ_{298} = 18 \text{ kJ mol}^{-1}, \quad \Delta S^\circ_{298} = 78 \text{ J K}^{-1} \text{ mol}^{-1} \)

Reaction Y: \( \frac{1}{2} \text{I}_2(s) + \frac{1}{2} \text{Br}_2(l) \rightleftharpoons \text{IBr}(g) \)  \( \Delta H^\circ_{298} = 41 \text{ kJ mol}^{-1}, \quad \Delta S^\circ_{298} = 124 \text{ J K}^{-1} \text{ mol}^{-1} \)

(a) Is reaction X, represented above, spontaneous under standard conditions? Justify your answer with a calculation.

(b) Calculate the value of the equilibrium constant, \( K_{eq} \), for reaction X at 25°C.

(c) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer.

(d) Explain why the standard entropy change is greater for reaction Y than for reaction X.

(e) Above what temperature will the value of the equilibrium constant for reaction Y be greater than 1.0? Justify your answer with calculations.

(f) For the vaporization of solid iodine, \( \text{I}_2(s) \rightarrow \text{I}_2(g) \), the value of \( \Delta H^\circ_{298} \) is 62 kJ mol\(^{-1}\). Using this information, calculate the value of \( \Delta H^\circ_{298} \) for the reaction represented below.

\[ \text{I}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ICl}(g) \]
(a) Is reaction $X$, represented above, spontaneous under standard conditions? Justify your answer with a calculation.

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

$$= (18 \text{ kJ mol}^{-1}) - (298 \text{ K})(0.078 \text{ kJ mol}^{-1} \text{ K}^{-1}) = -5 \text{ kJ mol}^{-1}$$

Reaction is spontaneous because $\Delta G^\circ < 0$.

(b) Calculate the value of the equilibrium constant, $K_{eq}$, for reaction $X$ at 25°C.

$$\ln K_{eq} = -\frac{\Delta G^\circ}{RT}$$

$$\ln K_{eq} = -\frac{-5 \text{ kJ mol}^{-1})(10^3 \text{ J kJ}^{-1})}{(8.31 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 2.019$$

$$K_{eq} = e^{2.019} = (7.5314) = 8$$
12) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer.

\[ \Delta G^\circ = -RT \ln K_{eq} = \Delta H^\circ - T\Delta S^\circ \Rightarrow \ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \]

Since \( \Delta H^\circ \) is positive, an increase in \( T \) will cause \(-\Delta H^\circ/RT\) to become a smaller negative number, therefore \( K_{eq} \) will increase.

**OR**

The reaction is endothermic (\( \Delta H = +18 \text{ kJ mol}^{-1} \)); an increase in temperature shifts the reaction to favor more products relative to the reactants, resulting in an increase in the value of \( K_{eq} \).

One point is earned for the correct choice with a correct explanation.

(d) Explain why the standard entropy change is greater for reaction \( Y \) than for reaction \( X \).

Both reaction \( X \) and reaction \( Y \) have solid iodine as a reactant, but the second reactant in reaction \( X \) is chlorine gas whereas the second reactant in reaction \( Y \) is liquid bromine. Liquids have lower entropies than gases, thus in reaction \( Y \) the reactants are more ordered (and have lower entropies) than in reaction \( X \). The products of both reaction \( X \) and reaction \( Y \) have about the same disorder, so the change in entropy from reactants to products is greater in reaction \( Y \) than in reaction \( X \).

One point is earned for a correct explanation.
(e) Above what temperature will the value of the equilibrium constant for reaction $Y$ be greater than 1.0? Justify your answer with calculations.

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \]
\[ K_{eq} = 1 \text{ when } \Delta G^\circ = 0 \Rightarrow T\Delta S^\circ = \Delta H^\circ \Rightarrow \]
\[ T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{41 \text{ kJ mol}^{-1}}{0.124 \text{ kJ mol}^{-1} \text{K}^{-1}} = 330 \text{ K} \]

So when $T > 330 \text{ K}$, $\Delta G^\circ < 0 \text{ kJ mol}^{-1} \Rightarrow K_{eq} > 1.0$

One point is earned for $\Delta G^\circ = 0$. One point is earned for the correct temperature.

(f) For the vaporization of solid iodine, $I_2(s) \rightarrow I_2(g)$, the value of $\Delta H_{298}^\circ$ is 62 kJ mol$^{-1}$. Using this information, calculate the value of $\Delta H_{298}^\circ$ for the reaction represented below.

\[ I_2(g) + Cl_2(g) \rightleftharpoons 2 ICl(g) \]

\begin{align*}
I_2(s) + Cl_2(g) & \rightleftharpoons 2 ICl(g) \quad \Delta H_{298}^\circ = 2 \times 18 \text{ kJ mol}^{-1} \\
I_2(g) & \rightleftharpoons I_2(s) \quad \Delta H_{298}^\circ = -62 \text{ kJ mol}^{-1} \\
I_2(g) + Cl_2(g) & \rightleftharpoons 2 ICl(g) \quad \Delta H_{298}^\circ = -26 \text{ kJ mol}^{-1} \\
\end{align*}

One point is earned for $\Delta H_{298}^\circ$ of either the first or second equation. One point is earned for the correct sum of the $\Delta H_{298}^\circ$ values.