Thermochemistry
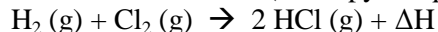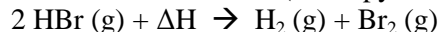
1. **Stoichiometry**

$$Enthalpy\ (J\ mol^{-1}) = \frac{heat\ (J)}{moles}$$

Exothermic Reaction (enthalpy is a product, energy is overall released, temperature of surrounding increases):
H_2 (g) + Cl_2 (g) → 2 HCl (g) + ΔH

Endothermic Reaction (enthalpy is a reactant, energy is overall absorbed, temperature of surroundings decreases):
2 HBr (g) + ΔH → H_2 (g) + Br_2 (g)

Thermal Equilibrium: When two substances have the same average kinetic energy.
An object DOES NOT have a certain amount of heat, rather heat is transferred or exchanged exothermically and endothermically.
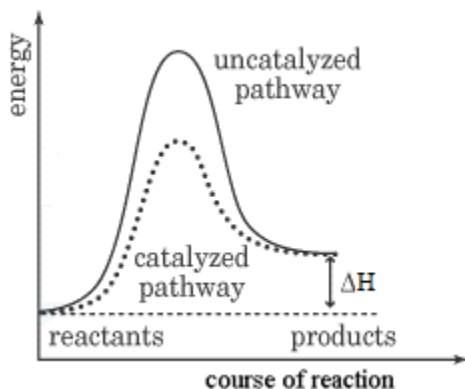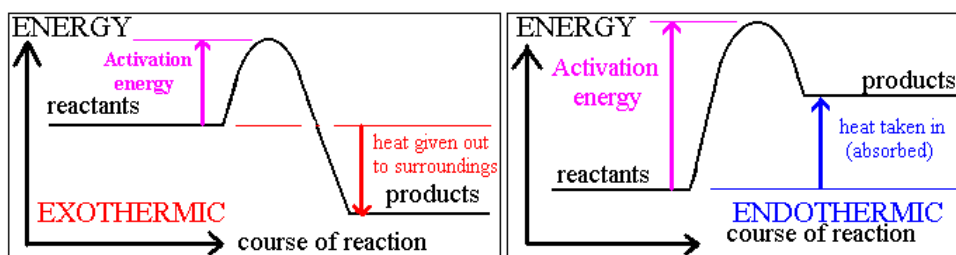
A catalyst lowers the activation energy and therefore speeds up the rate of a reaction by providing the reactants with an alternate pathway that has a lower activation energy. A catalyst lowers the activated complex only and is not consumed by the reaction and has no effect on the ΔH of the reaction. A catalyst also lowers the activation energy for both the forward and reverse reactions, therefore it has no effect on the equilibrium conditions.

2. Heat Calculations with Water

$q = mC\Delta T$

q = heat in J, m = mass, C = specific heat, $\Delta T = T_{final} - T_{initial}$
Specific Heat of water = 4.18 J g^{-1} mol^{-1}

$\Delta Hvap = \Delta Hcond$ = Energy absorbed to vaporize one mole = Energy released to condense one mole
$\Delta Hfusion = \Delta Hmelt$ = Energy released to freeze one mole = Energy absorbed to melt one mole

- **Example:**

$$Li \text{ (s)} + H_2O \text{ (l)} \rightarrow LiOH \text{ (aq)} + ½ H_2 \text{ (g)}$$

Placing 0.500 grams of lithium in water according to the balanced reaction above was able to increase the temperature of a small beaker of 100 grams of water placed above the reaction by 38.26°C.

(a) Calculate the number of moles of lithium used in the reaction.

$$moles = \frac{mass}{molar\ mass}$$

$$moles = \frac{0.500\ g}{6.941\ g\ mol^{-1}} = 0.0720\ mol$$

(b) Calculate the heat absorbed by the water.

$$q = mC\Delta T$$

$$q = (100\ g)(4.18\ J\ g^{-1}°C^{-1})(38.26°C) = 15{,}993\ J$$

(c) Calculate the enthalpy of the reaction in kJ mol^{-1}.

$$\Delta H = \frac{kJ}{mol}$$

$$\Delta H = \frac{15.993\ kJ}{0.0720\ mol} = 222\ kJ\ mol^{-1}$$
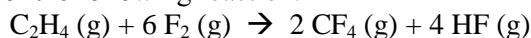
3. Hess's Law

Given a list of reactions
Flip reaction = flip the sign of ΔH
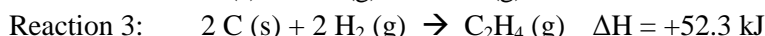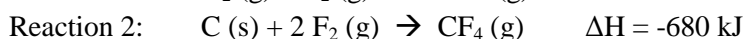Multiply or Divide reaction coefficients = Multiply or Divide ΔH
Add up all ΔH to get ΔHrxn

- **Example:**
  Calculate the enthalpy, ΔHrxn, for the following reaction:
  $$C_2H_4 \text{ (g)} + 6 \text{ } F_2 \text{ (g)} \rightarrow 2 \text{ } CF_4 \text{ (g)} + 4 \text{ } HF \text{ (g)}$$
  Given the reactions below:

Reaction 1:	H_2 (g) + F_2 (g) → 2 HF (g)	ΔH = -537 kJ
Reaction 2:	C (s) + 2 F_2 (g) → CF_4 (g)	ΔH = -680 kJ
Reaction 3:	2 C (s) + 2 H_2 (g) → C_2H_4 (g)	ΔH = +52.3 kJ
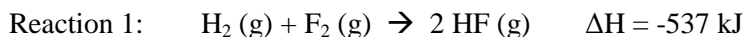
  Reaction 1: *The HF is on the product side in the target and sample reaction, therefore no flip*
  Reaction 1: *There are* 2 *moles of HF but you need* 4, *therefore multiply by* 2
  Reaction 1: $\Delta H = -537 \text{ } kJ \text{ } x \text{ } 2 = -1,074 \text{ } kJ$

  Reaction 2: *The* CF_4 *is on the product side in the target and sample reaction, therefore no flip*
  Reaction 2: *There is* 1 *mole of* CF_4 *but you need* 2, *theefore multiply by* 2
  Reaction 2: $\Delta H = -680 \text{ } kJ \text{ } x \text{ } 2 = -1,360 \text{ } kJ$

  Reaction 3: *The* C_2H_4 *is on the product side but needs to be on the reactant side, therefore flip*
  Reaction 3: *There is* 1 *mole of* C_2H_4 *present and* 1 *mole needed, therefore do not multiply*
  Reaction 3: : $\Delta H = = -52.3 \text{ } kJ$

  Note: *Do not look at the* F_2 *since it is in more than one reaction*

  $\Delta Hrxn = -1,074 \text{ } kJ + -1,360 \text{ } kJ + -52.3 \text{ } kJ = -2486.3 \text{ } kJ$

4. Standard Heats of Formation, ΔH_f

Given a heats of formation for substances
$\Delta H rxn = \Sigma H$ products $- \Sigma H$ reactants
$\Delta S rxn = \Sigma S$ products $- \Sigma S$ reactants
$\Delta G rxn = \Sigma G$ products $- \Sigma G$ reactants
(Don't forget to multiply by # of moles)
Remember, ΔH_f for a pure element is zero.

- **Example:**
  Given the heats of formation in the table below, calculate the enthalpy, $\Delta H rxn$, of the reaction:

$$2\ CH_3OH\ (g) + 3\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + 4\ H_2O\ (g)$$
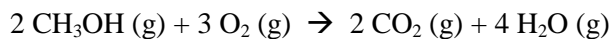
Substance	ΔH_f (kJ mol^{-1})
CH_3OH (g)	-201
CO_2 (g)	-394
H_2O (g)	-242

$$\Delta H_{rxn} = \sum H_f \text{ products} - \sum H_f \text{reactants}$$
$$\Delta H_{rxn} = [(-394 \times 2) + (-242 \times 4)] - [(-201 \times 2) + (0 \times 3)]$$
$$\Delta H_{rxn} = (-1756) - (-402) = -1{,}354 \text{ kJ}$$

5. **Bond Energy**

Given the energies to break bonds
Draw out all molecules (including the number of molecules)
(+) Energy for breaking bonds: Need energy to break bonds (**energy is absorbed to break bonds**)
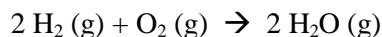(-) Energy for forming bonds: Release energy when forming bonds (**energy is released when forming bonds**)

Add up all energies of all bonds to get ΔHrxn
If the ΔHrxn is overall negative, the bond energies of the products are greater than the reactants or the energy to form bonds is greater than the energy to break bonds.

- **Example:**
  Given the bond energies in the table below, calculate the enthalpy, ΔHrxn, of the reaction:

$$2 H_2 (g) + O_2 (g) \rightarrow 2 H_2O (g)$$

Bond	Bond Energy (kJ mol^{-1})
H-H	436
O=O	499
O-H	463

Bonds Broken   Bonds Formed
2 H-H bonds = 2 x 436 kJ = 872 kJ   4 O-H bonds = 4 x -463 kJ = -1,852 kJ
1 O=O bond = 1 x 499 kJ = 499 kJ

Total energy to break bonds = 872 kJ + 499 kJ   Total energy to form bonds = -1,852 kJ
                                              = 1,371 kJ

ΔHrxn = 1,371 kJ + -1,852 kJ = -481 kJ
(Energy to form bonds or products is greater than the energy to break bonds or reactants)