What drives chemical reactions? How do they occur?
The first is answered by THERMODYNAMICS and the second by KINETICS.
Have already seen a number of “driving forces” for reactions that are PRODUCT-FAVORED.
- formation of a precipitate
- gas formation
- $\text{H}_2\text{O}$ formation (acid-base reaction)
- electron transfer in a battery

But energy transfer also allows us to predict reactivity.
In general, reactions that transfer energy to their surroundings are product-favored.

So, let us consider heat transfer in chemical processes.

Heat Energy Transfer in a Physical Process
$\text{CO}_2(\text{s}, -78 \, ^\circ\text{C}) \longrightarrow \text{CO}_2(\text{g}, -78 \, ^\circ\text{C})$

Heat flows into the SYSTEM (solid CO$_2$) from the SURROUNDINGS in an ENDOTHERMIC process.

$\Delta E = E(\text{final}) - E(\text{initial})$
$= E(\text{gas}) - E(\text{solid})$
Heat Energy Transfer in Physical Change

- Gas molecules have higher kinetic energy.
- Also, WORK is done by the system in pushing aside the atmosphere.

**FIRST LAW OF THERMODYNAMICS**

\[
\Delta E = q + w
\]

Energy is conserved!

**Endo- and Exothermic**

- Surroundings gain heat: \( q_{\text{system}} > 0 \)
  - System temperature \( T \) goes up
  - Surroundings temperature \( T \) goes down
  - Process is ENDOTHERMIC

- Surroundings lose heat: \( q_{\text{system}} < 0 \)
  - System temperature \( T \) goes down
  - Surroundings temperature \( T \) goes up
  - Process is EXOTHERMIC

**ENTHALPY**

- Most chemical reactions occur at constant \( P \), so
- Heat transferred at constant \( P = q_p \)
- \( q_p = \Delta H \) where \( H = \text{enthalpy} \)
- \( \Delta H = \text{heat transferred at constant } P = \Delta E \)
- \( \Delta H = \text{change in heat content of the system} \)
- \( \Delta H = H_{\text{final}} - H_{\text{initial}} \)

\[\Delta H = H_{\text{final}} - H_{\text{initial}}\]

- If \( H_{\text{final}} > H_{\text{initial}} \) then \( \Delta H \) is positive
  - Process is ENDOOTHERMIC
- If \( H_{\text{final}} < H_{\text{initial}} \) then \( \Delta H \) is negative
  - Process is EXOTHERMIC
Consider the decomposition of water:

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

Endothermic reaction — heat is a "reactant"

\[ \Delta H = +242 \text{ kJ} \]

Using Enthalpy:

Making H\(_2\) from H\(_2\)O involves two steps. Each step requires energy.

\[ \text{H}_2\text{O(l) + 44 kJ \rightarrow H}_2\text{(g) + 1/2 O}_2\text{(g)} \]

\[ \text{H}_2\text{O(g) + 242 kJ \rightarrow H}_2\text{(g) + 1/2 O}_2\text{(g)} \]

Example of Hess's Law:

If a reaction is the sum of 2 or more others, the net \( \Delta H \) is the sum of the \( \Delta H \)'s of the other reactions.

Using Enthalpy:

Calc. \( \Delta H \) for S(s) + 3/2 O\(_2\)(g) \rightarrow SO\(_3\)(g) knowing that:

\[ \text{S(s) + O}_2\text{(g) \rightarrow SO}_2\text{(g)} \quad \Delta H_1 = -320.5 \text{ kJ} \]
\[ \text{SO}_2\text{(g) + 1/2 O}_2\text{(g) \rightarrow SO}_3\text{(g)} \quad \Delta H_2 = -75.2 \text{ kJ} \]

The two equations add up to give the desired equation, so

\[ \Delta H_{\text{net}} = \Delta H_1 + \Delta H_2 = -395.7 \text{ kJ} \]
Standard Enthalpy Values
Most $\Delta H$ values are labeled $\Delta H^\circ$
Measured under standard conditions
$P = 1$ bar
Concentration $= 1$ mol/L
$T = \text{usually } 25 ^\circ C$
with all species in standard states
\( \text{e.g., } C = \text{graphite and } O_2 = \text{gas} \)

**Enthalpy Values**
Depend on how the reaction is written and on phases of reactants and products

- $\text{H}_2(g) + 1/2 \text{O}_2(g) \rightarrow \text{H}_2\text{O}(g)$
  \( \Delta H^\circ = -242 \text{ kJ} \)
- $2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g)$
  \( \Delta H^\circ = -484 \text{ kJ} \)
- $\text{H}_2\text{O}(g) \rightarrow \text{H}_2(g) + 1/2 \text{O}_2(g)$
  \( \Delta H^\circ = +242 \text{ kJ} \)
- $\text{H}_2(g) + 1/2 \text{O}_2(g) \rightarrow \text{H}_2\text{O(liquid)}$
  \( \Delta H^\circ = -286 \text{ kJ} \)

Using Standard Enthalpy Values
Use $\Delta H^\circ$’s to calculate enthalpy change for

- $\text{H}_2\text{O}(g) + \text{C(graphite)} \rightarrow \text{H}_2(g) + \text{CO(g)}$

(product is called “water gas”)

Using Standard Enthalpy Values
$\text{H}_2\text{O}(g) + \text{C(graphite)} \rightarrow \text{H}_2(g) + \text{CO(g)}$
From reference books we find
- $\text{H}_2(g) + 1/2 \text{O}_2(g) \rightarrow \text{H}_2\text{O}(g)$
  \( \Delta H^\circ \text{ of } \text{H}_2\text{O vapor} = -242 \text{ kJ/mol} \)
- $\text{C(s)} + 1/2 \text{O}_2(g) \rightarrow \text{CO(g)}$
  \( \Delta H^\circ \text{ of } \text{CO} = -111 \text{ kJ/mol} \)

$\Delta H^\circ$, standard molar enthalpy of formation
$\text{H}_2(g) + 1/2 \text{O}_2(g) \rightarrow \text{H}_2\text{O(g)}$
\( \Delta H^\circ \text{ (H}_2\text{O, g)} = -241.8 \text{ kJ/mol} \)
By definition, $\Delta H^\circ = 0$ for elements in their standard states.

NIST (Nat’l Institute for Standards and Technology) gives values of
$\Delta H^\circ = \text{standard molar enthalpy of formation}$
This is the enthalpy change when 1 mol of compound is formed from elements under standard conditions.
See Table 6.2 and Appendix L
Using Standard Enthalpy Values

\[ \begin{align*}
H_2O(g) & \rightarrow H_2(g) + 1/2 O_2(g) \quad \Delta H^\circ = +242 \text{ kJ} \\
C(s) + 1/2 O_2(g) & \rightarrow CO(g) \quad \Delta H^\circ = -111 \text{ kJ}
\end{align*} \]

\[ \begin{align*}
H_2O(g) + C & \rightarrow H_2(g) + CO(g) \\
& \Delta H^\circ_{\text{net}} = +131 \text{ kJ}
\end{align*} \]

To convert 1 mol of water to 1 mol each of \(\text{H}_2\) and CO requires 131 kJ of energy.

The “water gas” reaction is **ENDO**thermic.

In general, when **ALL** enthalpies of formation are known,

\[ \Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_{\text{prod}} - \sum \Delta H^\circ_{\text{react}} \]

Calculate \( \Delta H \) of reaction?

\[ \Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_{\text{prod}} - \sum \Delta H^\circ_{\text{react}} \]

\[ \Delta H^\circ_{\text{rxn}} = (-393.5 \text{ kJ}) + 2 (-241.8 \text{ kJ}) \]

\[ \Delta H^\circ_{\text{rxn}} = (-393.5 \text{ kJ}) + 2 (-201.5 \text{ kJ}) \]

\[ \Delta H^\circ_{\text{rxn}} = -675.6 \text{ kJ per mol of methanol} \]

**CALORIMETRY**

Measuring Heats of Reaction

- E transferred from system = E transferred to surroundings
- System = reaction
- Surround = water + “bomb”

**Calculate heat of combustion of octane.**

\[ C_8H_{18} + 25/2 O_2 \rightarrow 8 \text{ CO}_2 + 9 \text{ H}_2\text{O} \]

- Burn 1.00 g of octane
- Temp rises from 25.00 to 33.20°C
- Calorimeter contains 1200 g water
- Heat capacity of bomb = 837 J/K

Measuring Heats of Reaction

**CALORIMETRY**
Measuring Heats of Reaction
CALORIMETRY

Step 1  Calc. heat transferred from reaction to water.
\[ q = (4.184 \, \text{J/g} \cdot \text{K})(1200 \, \text{g})(8.20 \, \text{K}) = 41,170 \, \text{J} \]

Step 2  Calc. heat transferred from reaction to bomb.
\[ q = \text{(bomb heat capacity)}(\Delta T) = (837 \, \text{J/K})(8.20 \, \text{K}) = 6860 \, \text{J} \]

Step 3  Total heat evolved
\[ 41,170 \, \text{J} + 6860 \, \text{J} = 48,030 \, \text{J} \]

Heat of combustion of 1.00 g of octane = -48.0 kJ