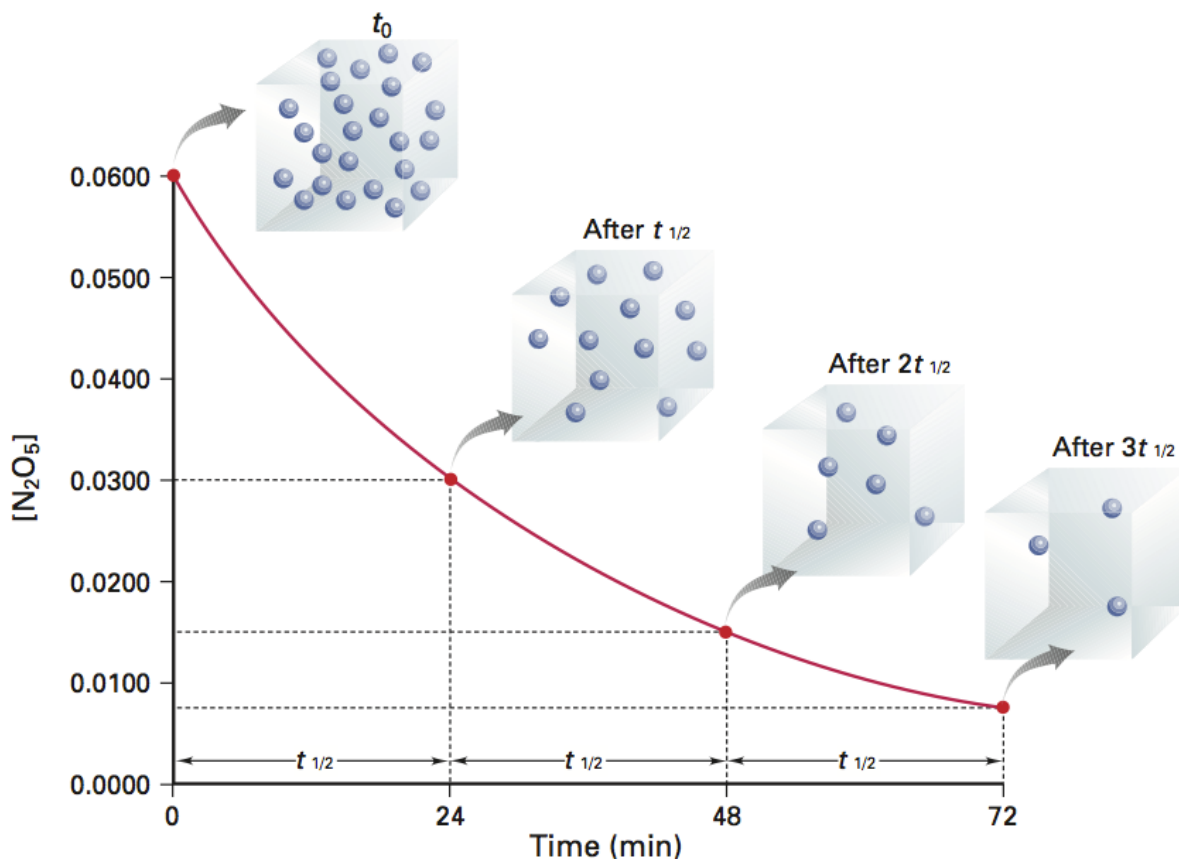# Grade 12 Chemistry

Energy Changes and Rates of Reaction

Class 10

Half-Life $t_{1/2}$

- Half-Life is the time that it takes for the reactant mass or concentration to decrease by one half of its initial value

- Half-Life tells you the speed of a reaction

$t_{1/2}$	Amount (%)
0	100%
1	50%
2	25%
3	12.5%
4	6.25%
5	3.125%

Half-Life for Reaction Orders

First-Order Reaction   **Second-Order Reaction**   **Zeroth-Order Reaction**

$$t_{\frac{1}{2}} = \frac{0.693}{k} \qquad t_{\frac{1}{2}} = \frac{1}{k[\text{A}]_0} \qquad t_{\frac{1}{2}} = \frac{[\text{A}]_0}{2k}$$
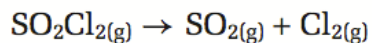
- Half-Life for a first-order reaction is independent of the initial concentration of the reactants; only depends on k

STOP Checkpoint STOP

The decomposition of sulfuryl chloride, SO_2Cl_2, is a first-order reaction.

$SO_2Cl_{2(g)} \rightarrow SO_{2(g)} + Cl_{2(g)}$

Rate $= k[SO_2Cl_2]$

At 320°C, the rate constant is 2.2×10^{-5} s^{-1}.

(a) Calculate the half-life of the reaction, in hours.

(b) How long does the sulfuryl chloride take to decrease to $\frac{1}{8}$ of its original concentration?
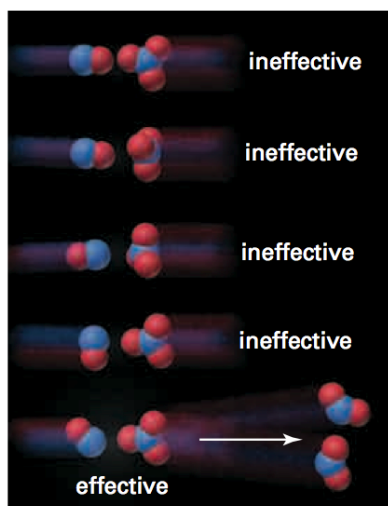
Factors that Affect Reaction Rate

Collision Theory – In order for a reaction to occur, reacting particles must collide with one another

1. Concentration – how frequently the reactant molecules collide
2. Surface Area – more collisions can occur
3. Orientation
4. Sufficient Energy – temperature
5. Catalyst

Orientation

$$NO(g) + NO_3(g) \rightarrow NO_2(g) + NO_2(g)$$
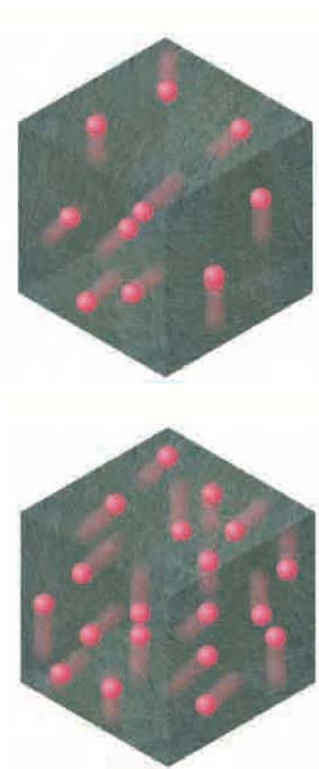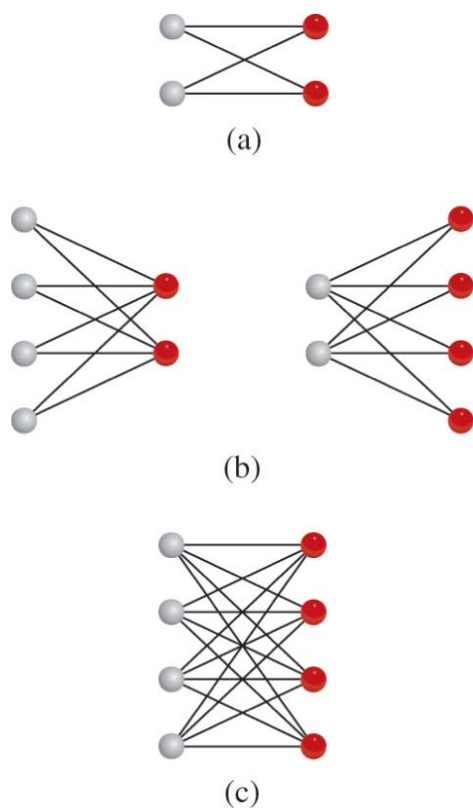
- Only a certain orientation (collision geometry) of the NO and NO_3 will cause the formation of the products

Activation Energy

- Every chemical reaction has an **activation energy (E_a)** or the minimum energy required for a successful reaction
- Depends on the kinetic energy of the colliding particles (temperature)
- If you plot the number of collisions you get a Maxwell-Boltzmann distribution curve
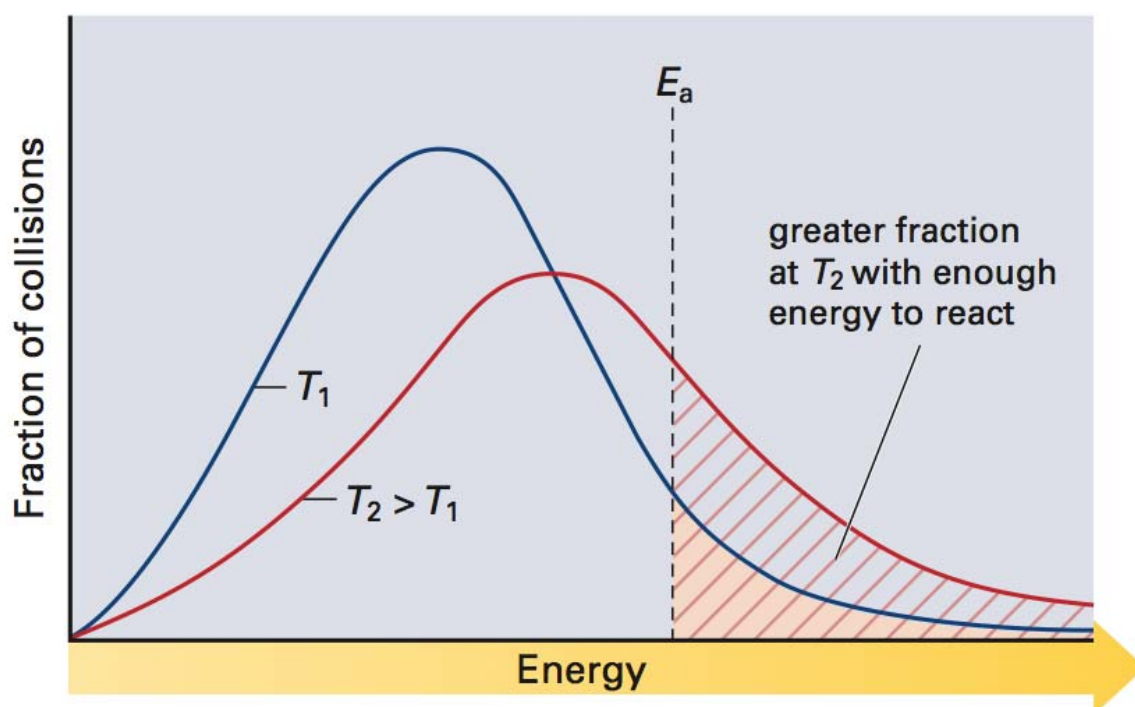
Transition State Theory

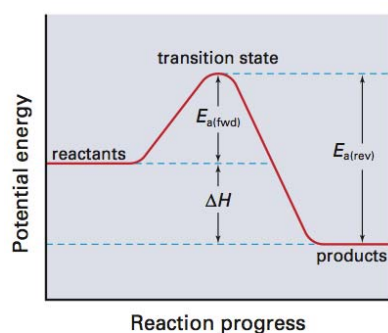- Explains what happens when molecules collide in a reaction and examines the transition from reactants to products

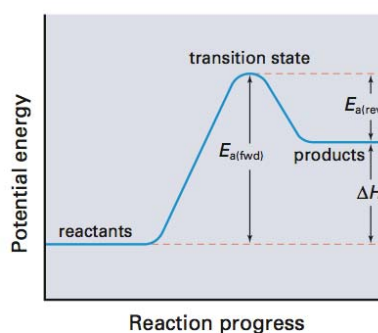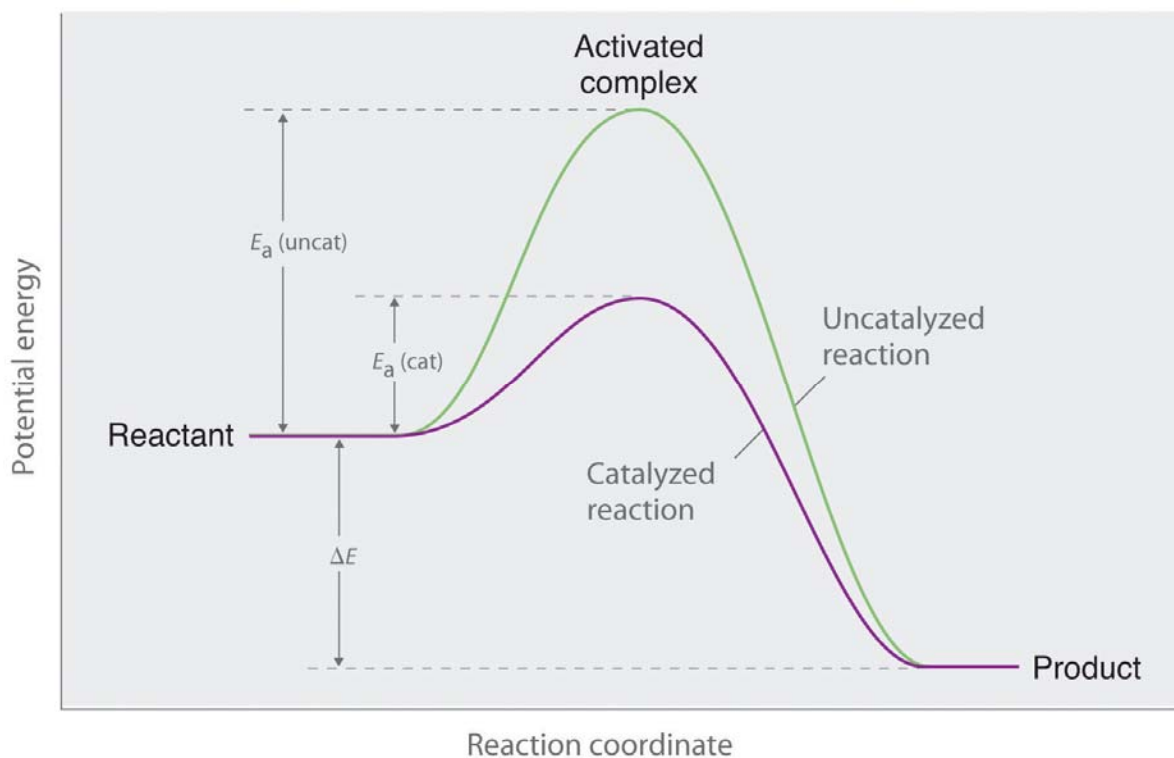**Figure 6.12** A potential energy diagram for an exothermic reaction

Figure 6.13 A potential energy diagram for an endothermic reaction

- If the reactants possess enough energy, they reach a short-lived **transition state**, consisting of an **activated complex**

- Note: You cannot predict the activation energy of a reaction from its enthalpy change; Thermodynamics and kinetic factors do not affect each other
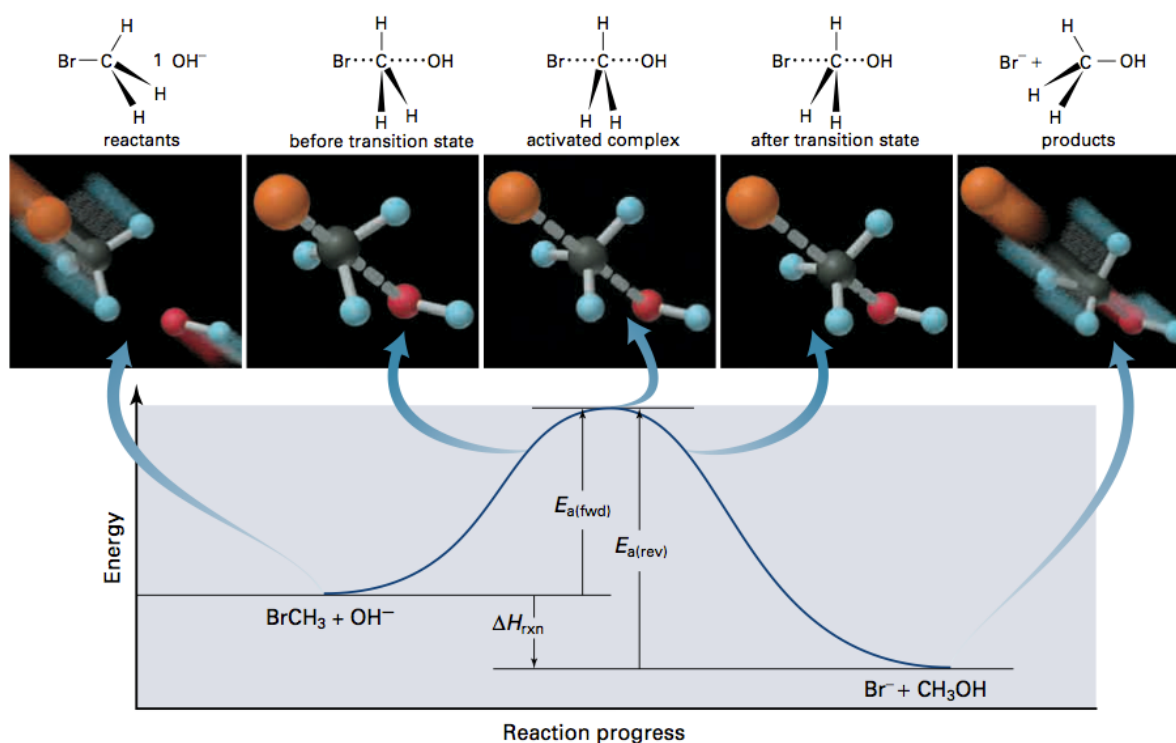
Catalyst

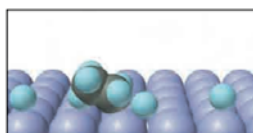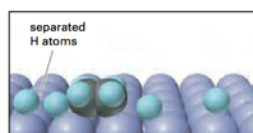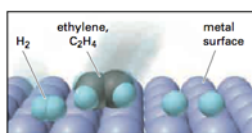- Catalyst functions to lower the activation energy of the rate-determining step, thereby making the reaction proceed faster

- Lowered activation energy = faster reaction

- A catalyst remains unchanged at the end of the reaction and are not included in the overall reaction equation

Activated complex

Potential energy

E_a (uncat)

E_a (cat)

Reactant

Uncatalyzed reaction

Catalyzed reaction

ΔE

Product

Reaction coordinate

- **Homogenous Catalysts** – exist in the same phase as the reactants

$$(CH_3)_2CHOH_{(aq)} + HCl_{(aq)} \xrightarrow{ZnCl_{2(aq)}} (CH_3)_2CHCl_{(aq)} + H_2O_{(\ell)}$$
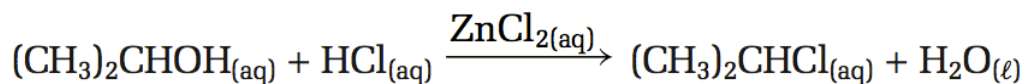
- **Heterogeneous Catalysts** – exist in a phase different from the reactants

$$H_2C = CH_{2(g)} + H_{2(g)} \xrightarrow{Pd_{(s)}} H_3C — CH_{3(g)}$$

① H_2 and C_2H_4 approach and bond to metal surface.

② Rate-limiting step is H—H bond breakage.

③ One H atom bonds to C_2H_4.

④ Another C—H bond forms, and C_2H_6 leaves the surface.
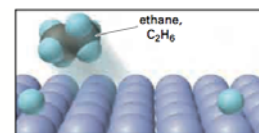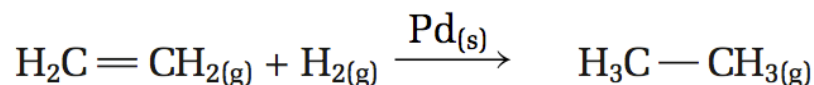
Checkpoint

Consider the following reaction.

$$AB + C \rightarrow AC + B \quad \Delta H = +65 \text{ kJ}, \ E_{a(rev)} = 34 \text{ kJ}$$
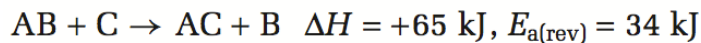
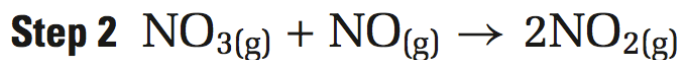Draw and label a potential energy diagram for this reaction. Calculate and label $E_{a(fwd)}$. Include a possible structure for the activated complex.

Reaction Mechanisms

- A series of steps that make up an overall reaction
- Each step is called an **elementary reaction**

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$

Step 1 $\quad NO_{(g)} + O_{2(g)} \rightarrow NO_{3(g)}$

Step 2 $\quad NO_{3(g)} + NO_{(g)} \rightarrow 2NO_{2(g)}$
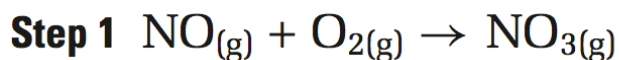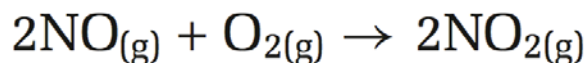
- Reaction intermediates – formed and consumed

Elementary Reactions

- The rate law for elementary reactions do not need to be determined by experiments
- The exponents in the rate law equation are the same as the stoichiometric coefficients for each reactant in the chemical equation

Table 6.3 Elementary Reactions and Their Rate Laws

Elementary reaction	Rate law
A → products	Rate = $k[A]$
A + B → products	Rate = $k[A][B]$
2A → products	Rate = $k[A]^2$
2A + B → products	Rate = $k[A]^2[B]$

Reaction Mechanism: An Analogy

Overall Reaction:

Dirty Dish → Clean and Dry Dish

Elementary steps:

1) Dirty Dish → Soapy Dish
2) Soapy Dish → Rinsed Dish
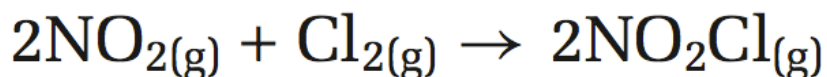3) Rinsed Dish → Clean and Dry Dish

Intermediates – materials that are made and consumed

Rate-Determining Step

1) Dirty Dish → Soapy Dish   5 dishes/min
2) Soapy Dish → Rinsed Dish   8 dishes/min
3) Rinsed Dish→ Dry Dish   3 dishes/min

The rate of the overall reaction depends on the slowest step:

The slowest step in a process determines the overall reaction rate

$$2NO_{2(g)} + Cl_{2(g)} \rightarrow 2NO_2Cl_{(g)}$$

Experimental Rate Law: $Rate = k[NO_2][Cl_2]$

Elementary Reactions:

Step 1 $NO_{2(g)} + Cl_{2(g)} \rightarrow NO_2Cl_{(g)} + Cl_{(g)}$ (slow)

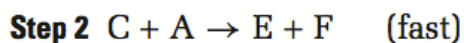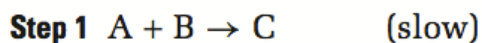**Step 2** $NO_{2(g)} + Cl_{(g)} \rightarrow NO_2Cl_{(g)}$ (fast)

Checkpoint

A chemist proposes the following reaction mechanism for a certain reaction.

Step 1 $A + B \rightarrow C$ (slow)

Step 2 $C + A \rightarrow E + F$ (fast)

**(a)** Write the equation for the chemical reaction that is described by this mechanism.

(b) Write a rate law equation that is consistent with the proposed mechanism.

Will the reaction go?

- In chemical kinetics, we ask

  "How fast does the reaction go?"

- In thermochemistry, we ask

  "Will the reaction go?"

- Reaction that *does* go under a given set of conditions is called a **spontaneous** reaction
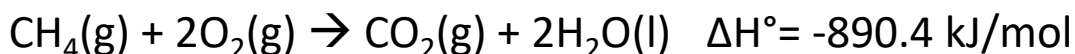
Spontaneous vs. Nonspontaneous
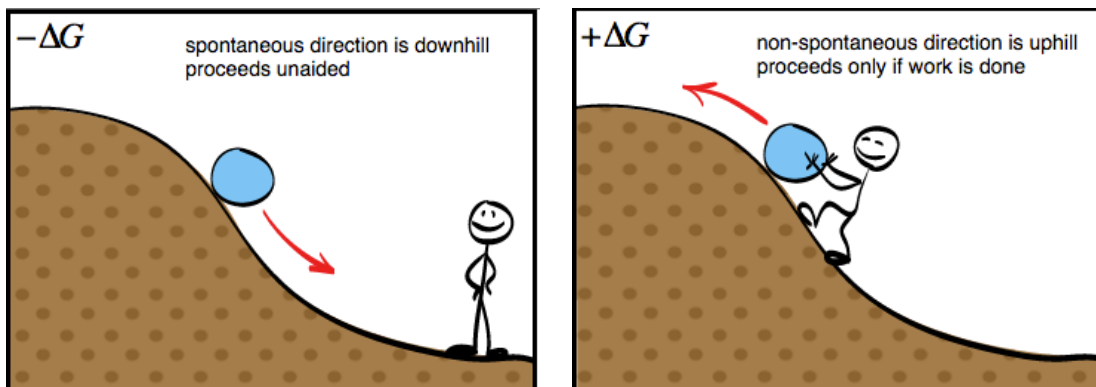
- Spontaneous processes occur to decrease the energy of a system

- A large number of exothermic reactions are spontaneous

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H° = -890.4$ kJ/mol

- But consider…

 $H_2O(s) \rightarrow H_2O(l)$ $\Delta H° = +6.01$ kJ/mol

- Therefore, an exothermic reaction is not always spontaneous
- **Enthalpy** alone cannot determine spontaneity

- **Temperature** also determines whether or not a reaction is spontaneous

$$Hg_{(\ell)} + \frac{1}{2}O_{2(g)} \rightleftharpoons HgO_{(s)} \quad \Delta H = \pm 90.8 \text{ kJ}$$

- From left to right, the reaction is exothermic but above 400°C, the reverse reaction is favourable
- Direction of the reaction depends on temperature
- **Temperature and Enthalpy** alone cannot determine spontaneity

Entropy (S)
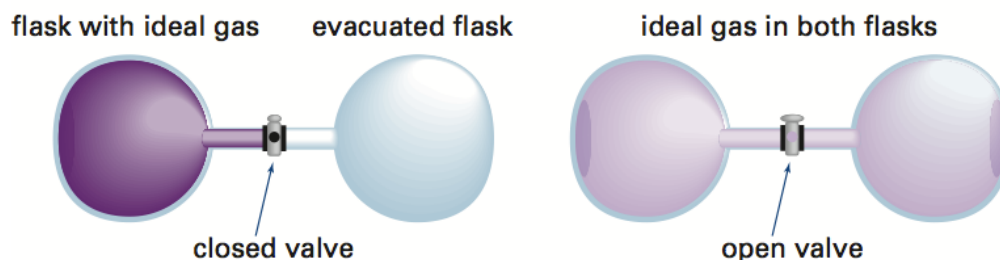
- A measure of how spread out or dispersed the energy of a system is among the different possible ways that the system can contain energy
- Units: J/K

Second Law of Thermodynamics

- The total entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process

Spontaneous Process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$

Equilibrium Process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$
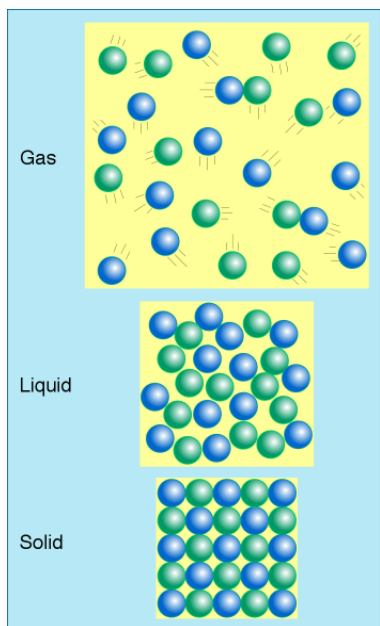
- The larger the value of S, the greater the molecular dispersal

- Change in Entropy:

$$\Delta S = S_{final} - S_{initial}$$

  - If ΔS is positive, system has become more dispersed
  - If ΔS is negative, system has become less dispersed

Checkpoint

Predict whether ΔS is likely to be positive or negative for each of the following reactions.

a) $H_2C=CH_2(g) + Br_2(g) \rightarrow CH_2BrCH_2Br(l)$

b) $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$

c) $C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$

Gibbs Free Energy

- To determine the spontaneity of a reaction, we must consider enthalpy (ΔH), temperature (T) and entropy (ΔS)

Gibbs Free Energy   **ΔG = ΔH – TΔS**

where T is temperature in K

- If   ΔG < 0 (-) Spontaneous

ΔG = 0 Equilibrium

ΔG > 0 (+) Nonspontaneous

ΔH	ΔS	ΔG	Reaction is...?
-	+	-	Spontaneous
+	+	- at high T	Spontaneous
		+ at low T	Nonspontaneous
-	-	+ at high T	Nonspontaneous
		- at low T	Spontaneous
+	-	+	Nonspontaneous

STOP **Checkpoint** STOP

a) Is the reaction $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ spontaneous under standard conditions at 25°C? $\Delta H° = 178.3$ kJ $\Delta S° = 160$ J/K

a) What must be true about a spontaneous, endothermic reaction?

   a) ΔH is negative   c) ΔS is positive

   b) ΔG is positive   d) ΔS is negative