Lecture 2. Thermodynamics. Kinetics.

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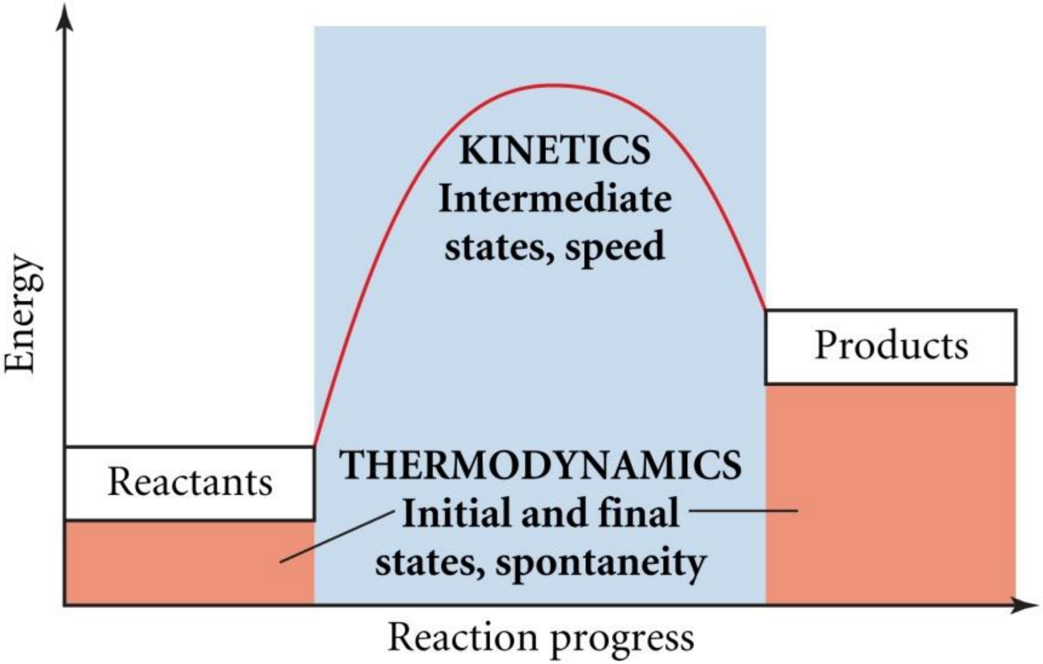
Entropy and Free Energy

How to predict if a reaction can occur at a reasonable rate? KINETICS

How to predict if a reaction can occur, given enough time?

THERMODYNAMICS



Thermodynamics is the study of energy relationships that involve heat, mechanical work, and other aspects of energy and heat transfer.

Work, Power, Energy

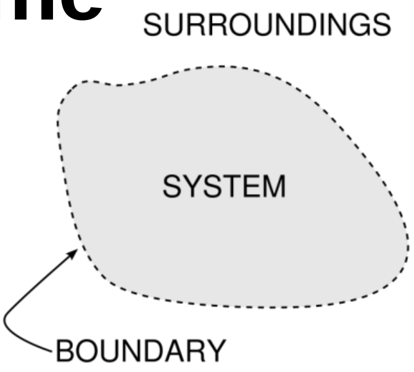
Work (J)

- Measure of motion accomplishment of a system due to the action of a force over a distance and time (*Dynamics*)
- *(…) work expresses the useful effect that a motor is capable of producing. This effect can always be linked to the elevation of a weight to a certain height(…) the product of the weight multiplied by the height to which it is raised" (Sadi* Carnot)

Power (W=J/s)

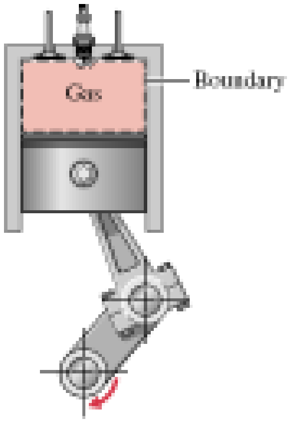
- The rate at which work Energy (J) is done
- Amount of work that can be accomplished by a force
- Is the capacity of a system to perform work

Closed Systems and Control Volume



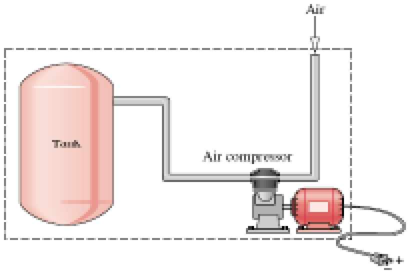
System is a set of interacting or interdependent entities, real or abstract, forming an integrated whole

Closed System *is a s*ystem that is isolated from its surroundings



☐ **<u>In thermodynamics</u>**

- a ***closed system can exchange heat and work (energy), but not matter***, with its surroundings
- ***Isolated system cannot exchange*** anything



Control Volume is a region of space through which mass flows

Property, State and Process

Property – macroscopic characteristic of a system

- ***Extensive properties***
  - The value for the overall system is the sum of the values for its parts (mass, volume, energy)
- ***Intensive properties***
  - The values are not additive, may vary from one place to the other at any time (pressure, temperature, specific volume)

State – a condition of a system, described by the properties

- usually a snapshot in time x(t)=(P,T)

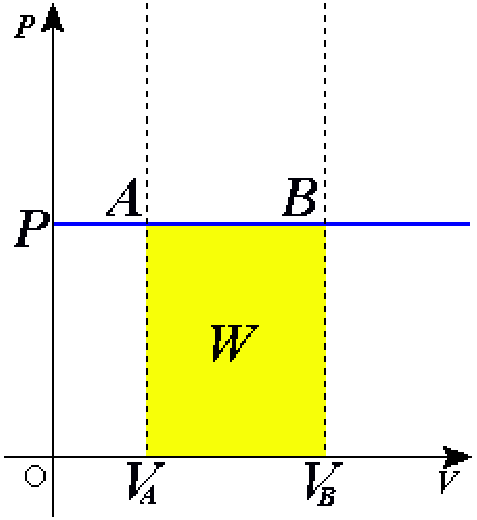
Process – change of properties and therefore state of the system

- brings the system from x(t) to x(t+1)

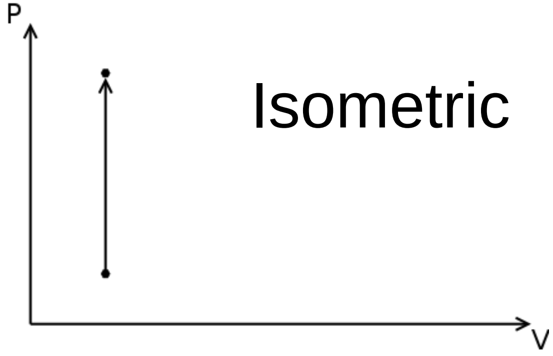
- Isothermal process → the process takes place at constant temperature
  (e.g. freezing of water to ice at –10 ℃)
- Isobaric → constant pressure
  (e.g. heating of water in open air→ under atmospheric pressure)
- Isochoric → constant volume
  (e.g. heating of gas in a sealed metal container)
- Reversible process → the system is close to equilibrium at all times (and infinitesimal alteration of the conditions can restore the universe (system + surrounding) to the original state.
- Cyclic process → the final and initial state are the same. However, q and w need not be zero.
- Adiabatic process → dq is zero during the process (no heat is added/removed to/from the system)

❑ A combination of the above are also possible: e.g. ‘reversible adiabatic process’.

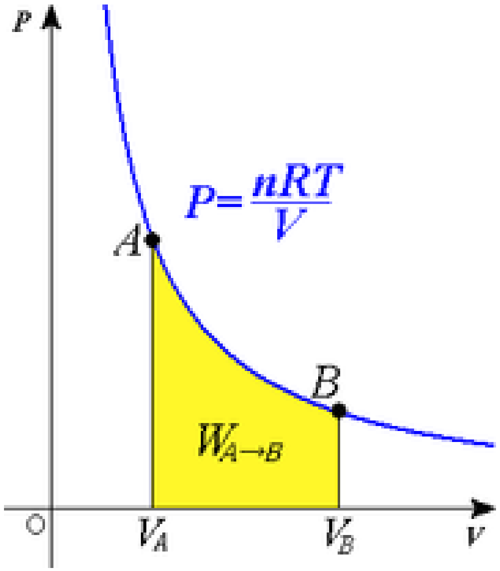
Different Processes



Isobaric

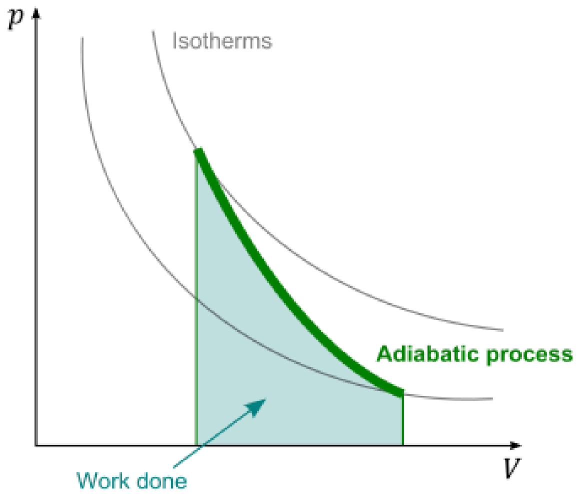


Isometric



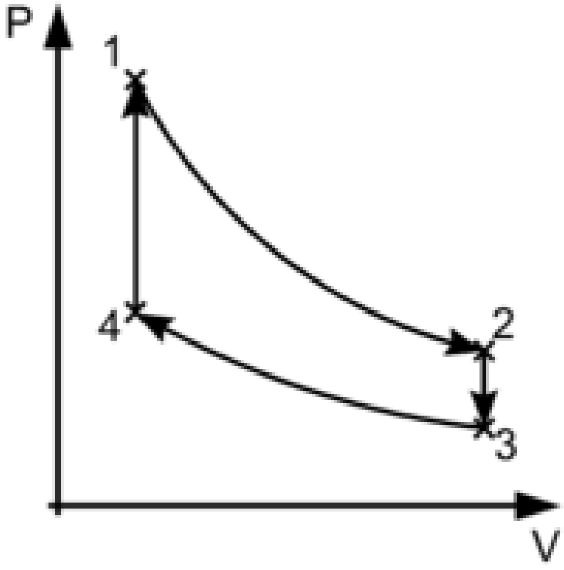
Isothermal

$\Delta T = 0$ but $Q \neq 0$



Adiabatic

$\Delta T \neq 0$ but $Q = 0$



Cyclic

If clockwise – heat engine

If counterclockwise – heat pump

Reversible and Irreversible Processes

Reversible (ideal)

- system and surroundings can be restored to the initial state from the final state without producing any changes in the thermodynamics properties
  - it should occur infinitely slowly due to infinitesimal gradient
  - all the changes in state occurred in the system are in thermodynamic equilibrium with each other

Irreversible (natural)

- All processes in nature are irreversible
  - Finite gradient between the two states of the system
    - heat flow between two bodies occurs due to temperature gradient between the two bodies

Thermodynamics and Kinetics

Diamond is thermodynamically favored to convert to graphite, but not kinetically favored.

Paper burns — a product-favored reaction. Also kinetically favored once reaction is begun.

The thermodynamic potentials **U, H, F** and **G** are state functions. If we know these functions then all the thermodynamic properties of a system can be calculated by differentiation alone.

Consider $dU(S,V) = TdS - PdV$

The extensive variables **S,V** are taken as independent. We say that **U** is a generating function having as its natural variables **S** and V. Canonically conjugate pairs are (**$-P$, V**) and (**T, S**). The first pair are mechanical variables and the second pair are thermal variables.

Laws of thermodynamics

0th Definition of temperature

- Systems at different temperatures exchange energy until reaching a thermal equilibrium

1st Conservation of energy

- heat is a form of energy

2nd Entropy of an isolated system never decreases

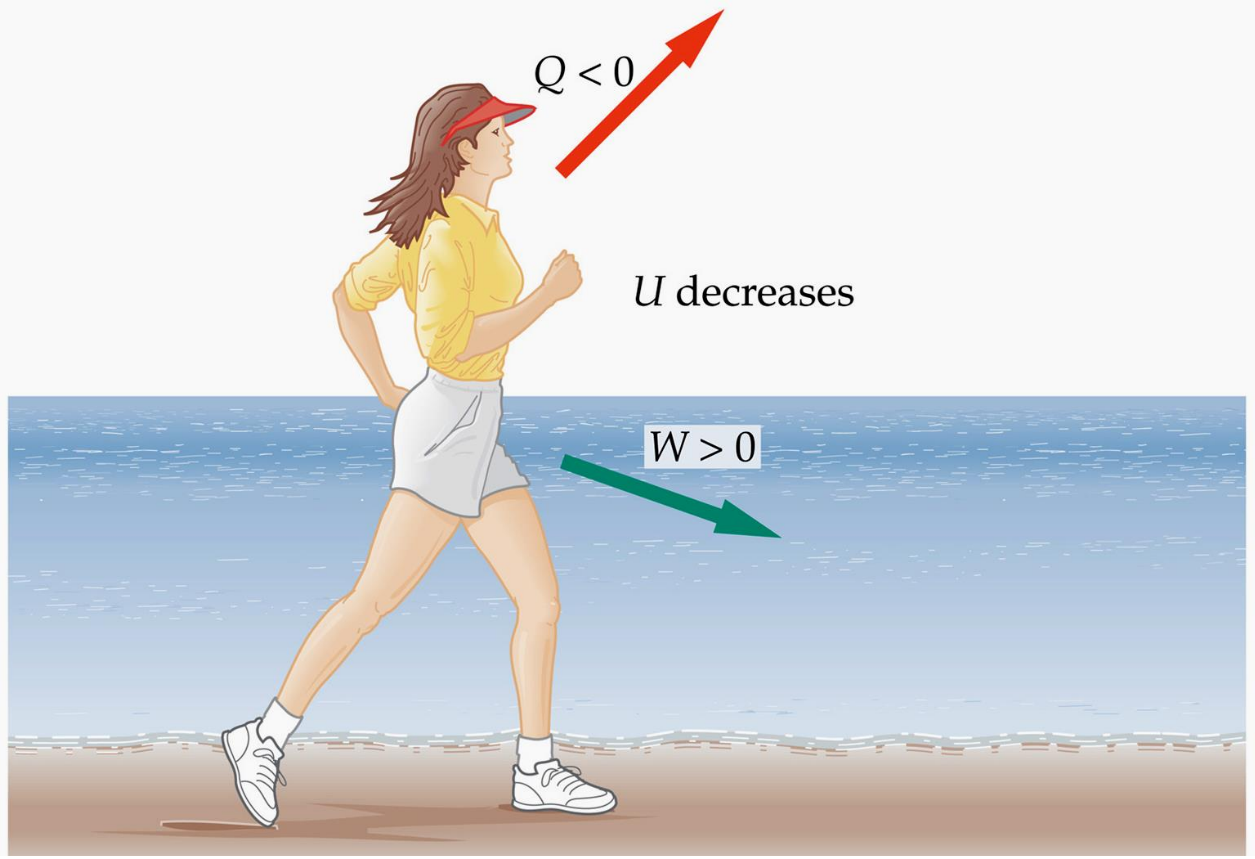
- perpetual motions of machines is impossible

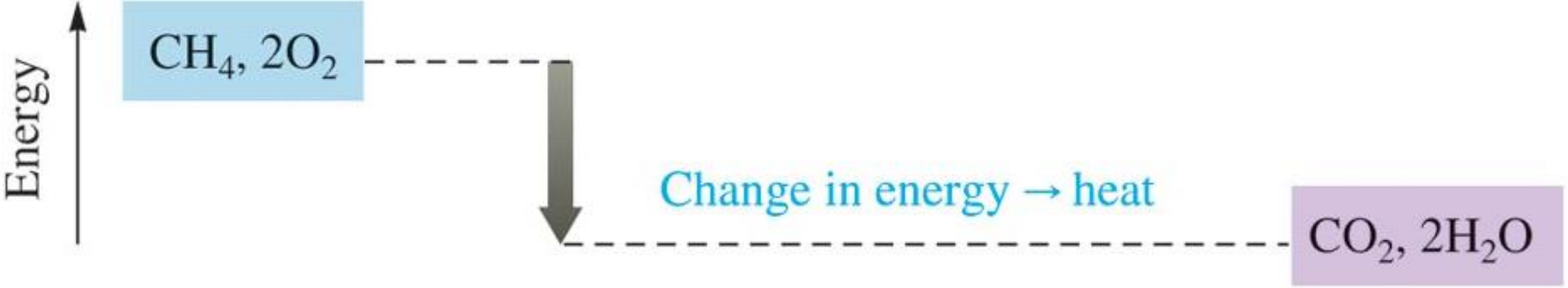
3rd Entropy at absolute zero temperature (0 K)

- it is impossible to cool a system until zero

The First Law of Thermodynamics

The internal energy of the system depends only on its temperature. The work done and the heat added, however, depend on the details of the process involved.





I. Conservation of Energy

First Law of Thermodynamics = energy cannot be created or destroyed, only converted between different forms

Example: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O + \text{energy}$

a) Reaction gives off energy as heat
b) Potential energy stored in chemical bonds is lowered
c) Total energy is unchanged

1. Uses and Shortcomings
   a) Lets us keep track of energy flow in processes
   b) Does not tell us if or why a given process occurs
   c) Does not tell us direction of a chemical reaction

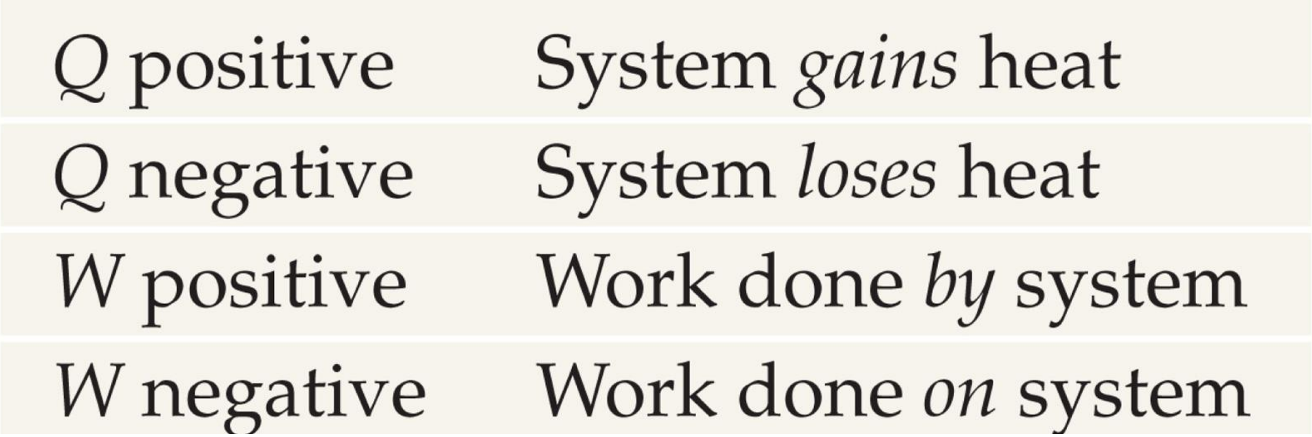
The First Law of Thermodynamics

The change in a system's internal energy is related to the heat Q and the work W as follows:

$$\Delta U = Q - W$$

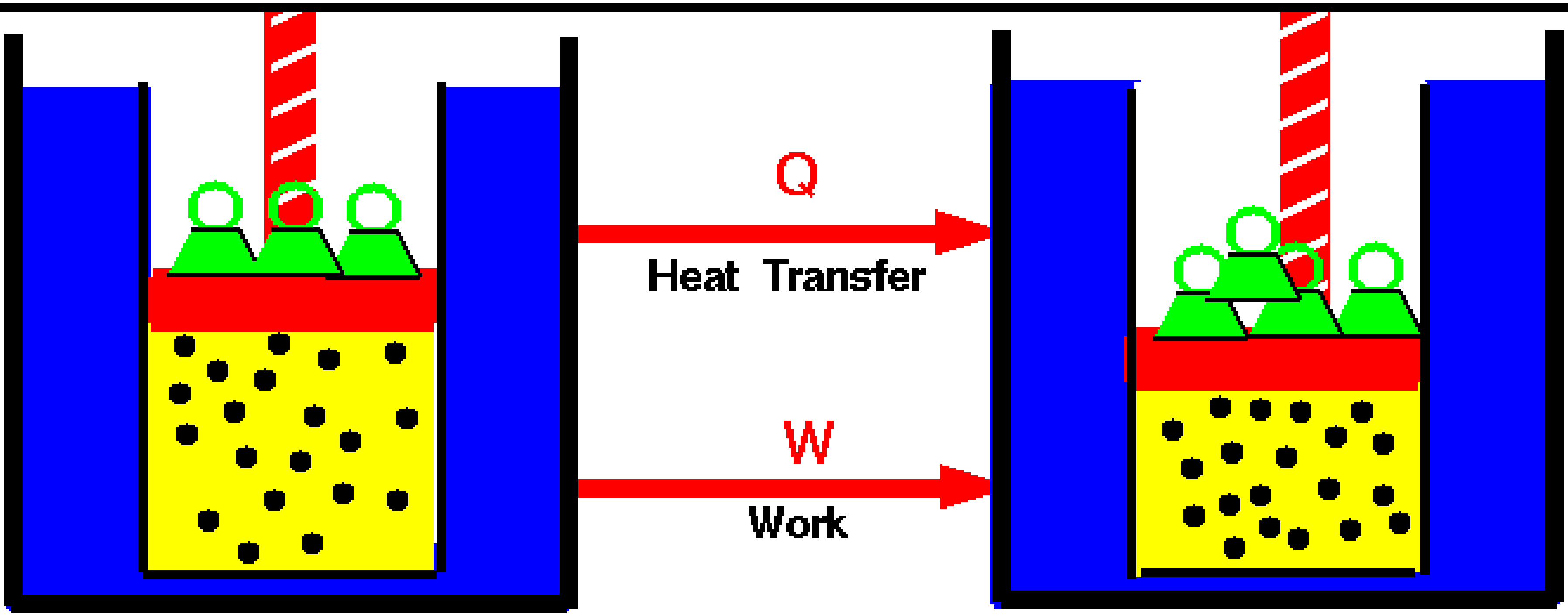
It is vital to keep track of the signs of Q and W.

The first law of thermodynamics when heat is added into a system it can either 1) change the internal energy of the system (i.e. make it hotter) or 2) go into doing work. ***Q=W +ΔU.***



Q positive	System *gains* heat
Q negative	System *loses* heat
W positive	Work done *by* system
W negative	Work done *on* system

First Law of Thermodynamics



E = Internal Energy

$$E_2 - E_1 = Q - W$$

Any thermodynamic system in an equilibrium state possesses a state variable called the internal energy (E). Between any two equilibrium states, the change in internal energy is equal to the difference of the heat transfer into the system and work done by the system.

Enthalpies of Formation

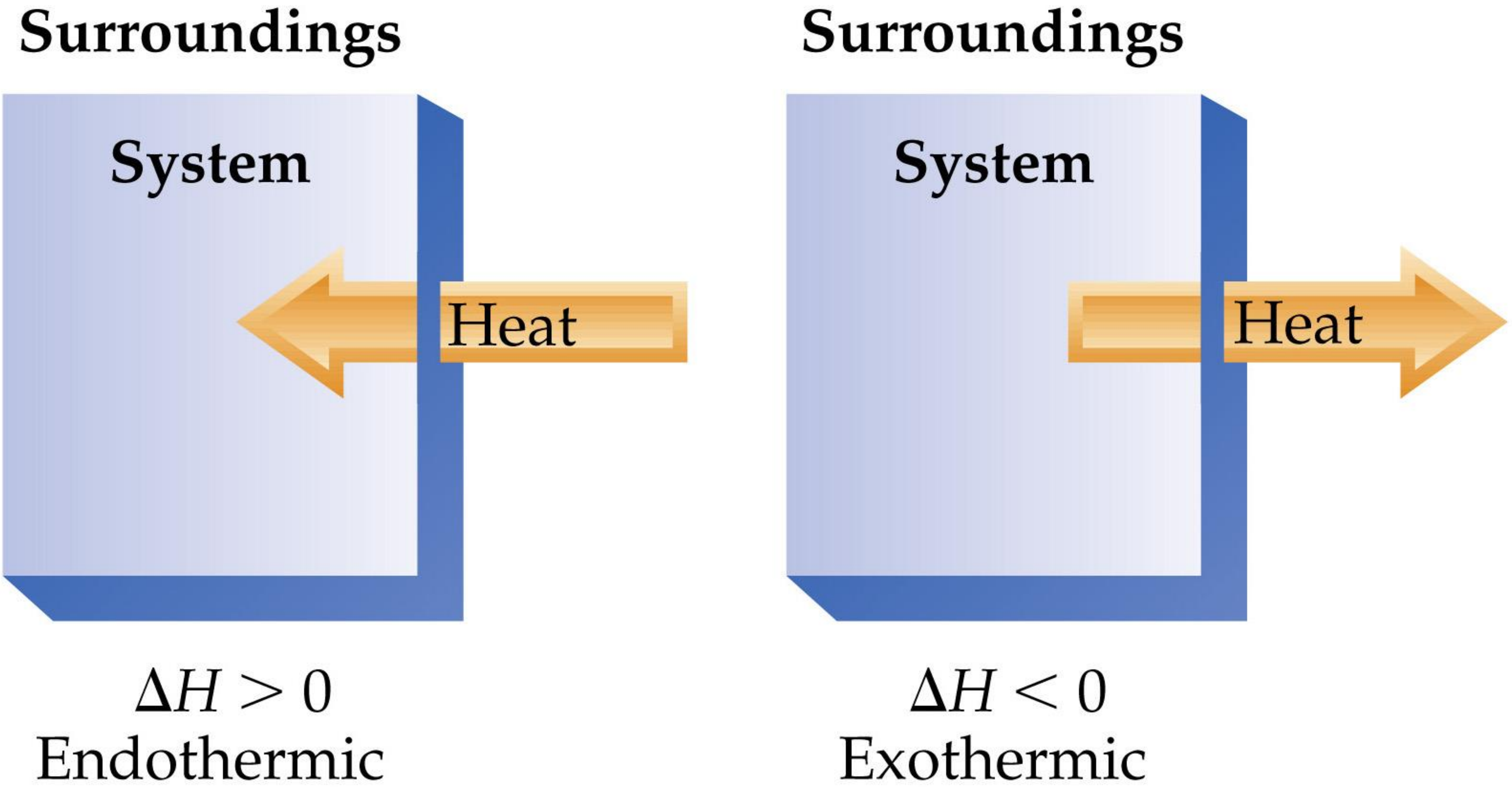
- ***Standard State Conditions***
- Temperature - 25^{o}C or 298K
- Pressure – 1.00 atm
- Element in its stable state

- If 1 mol of compound is formed from its constituent elements, then the enthalpy change for the reaction is called the enthalpy of formation, $\Delta H^o{}_f$.
- ***Standard conditions*** (standard state): Most stable form of the substance at 1 atm and 25 ^{o}C (298 K).
- ***Standard enthalpy***, ΔH^o, is the enthalpy measured when everything is in its standard state.
- ***Standard enthalpy of formation***: 1 mol of compound is formed from substances in their standard states.

Enthalpy => Heat of Reaction

$$\Delta H^\circ_{\text{rxn}} = \sum n \cdot \Delta H^\circ_f(\text{products}) - \sum m \cdot \Delta H^\circ_f(\text{reactants})$$

Note: n & m are stoichiometric coefficients



Calorimetry

Heat Capacity and Specific Heat

- ***Calorimetry*** = measurement of heat flow.
- ***Calorimeter*** = apparatus that measures heat flow.
- ***Heat capacity*** = the amount of energy required to raise the temperature of an object (by one degree).
- ***Molar heat capacity*** = heat capacity of 1 mol of a substance.
- ***Specific heat*** = specific heat capacity = heat capacity of 1 g of a substance.

$$q = (\text{specific heat}) \times (\text{grams of substance}) \times \Delta T$$

Chemical process

$$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g) + 394\ kJ$$

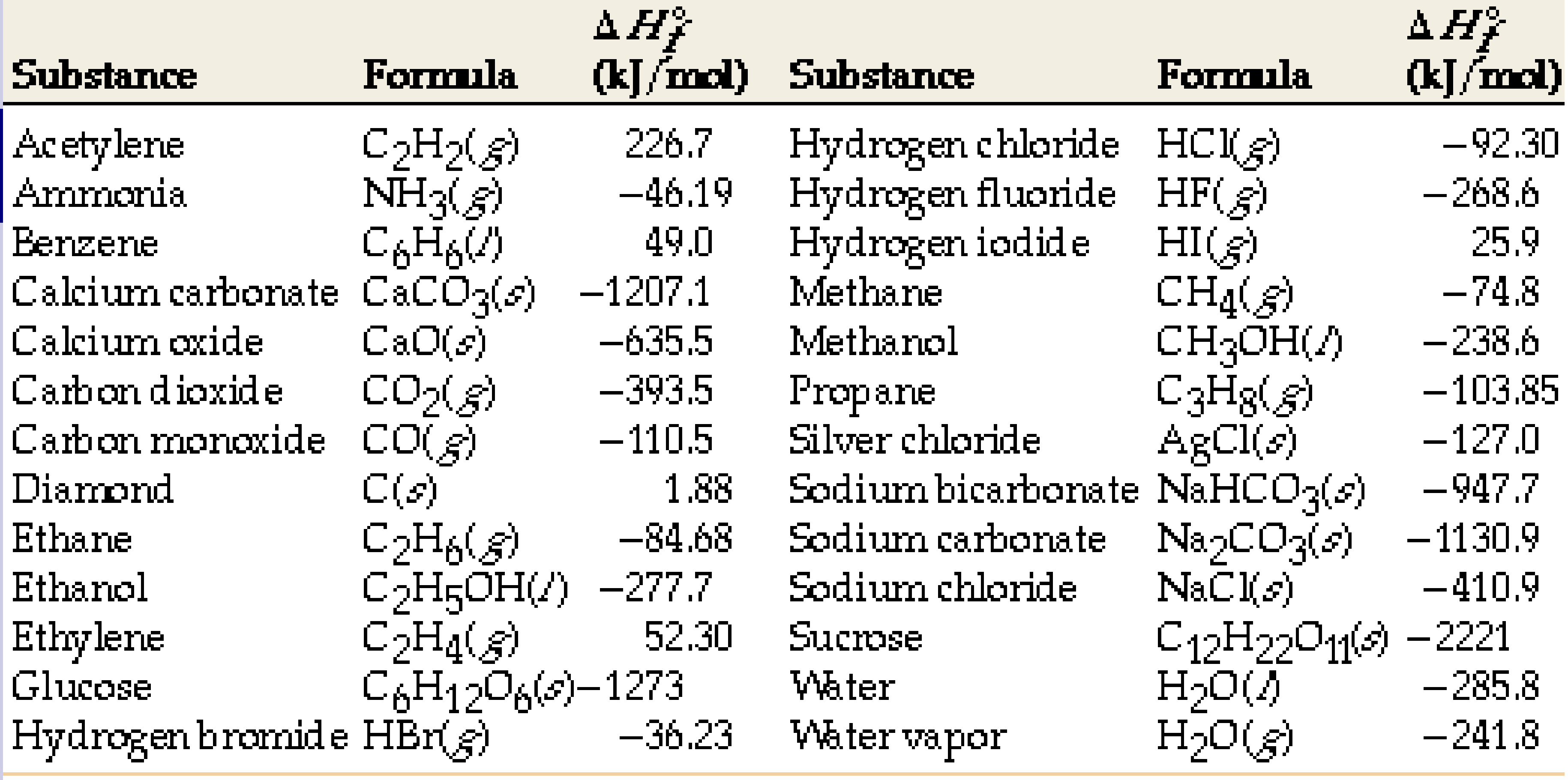
$$\Delta H^o_f = -394\ kJ/mole$$

This is the standard molar enthalpy of formation for the formation of one mole substance from its elements in their standard states.

$\Delta H^o_f = 0$ kJ/mole for free elements

Enthalpies of Formation

The enthalpy of formation, ΔH_f, or heat of formation, is defined as the change in enthalpy when one mole of a compound is formed from its stable elements.



Substance	Formula	ΔH_f° (kJ/mol)	Substance	Formula	ΔH_f° (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	−92.30
Ammonia	$NH_3(g)$	−46.19	Hydrogen fluoride	$HF(g)$	−268.6
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	−1207.1	Methane	$CH_4(g)$	−74.8
Calcium oxide	$CaO(s)$	−635.5	Methanol	$CH_3OH(l)$	−238.6
Carbon dioxide	$CO_2(g)$	−393.5	Propane	$C_3H_8(g)$	−103.85
Carbon monoxide	$CO(g)$	−110.5	Silver chloride	$AgCl(s)$	−127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	−947.7
Ethane	$C_2H_6(g)$	−84.68	Sodium carbonate	$Na_2CO_3(s)$	−1130.9
Ethanol	$C_2H_5OH(l)$	−277.7	Sodium chloride	$NaCl(s)$	−410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	−2221
Glucose	$C_6H_{12}O_6(s)$	−1273	Water	$H_2O(l)$	−285.8
Hydrogen bromide	$HBr(g)$	−36.23	Water vapor	$H_2O(g)$	−241.8

$2C(s) + 1/2\ O_2(g) + 3\ H_2\ (g) \dashrightarrow C_2H_5OH(l)$ $\qquad \Delta H_f^o = -277.69$ kJ

This equation can be written as the sum of the following three equations

$C_3H_8(g) \text{ --> } 3C(s) + 4H_2(g) \qquad \Delta H_1 = - \Delta H_f^o\,(C_3H_8(g))$

$+ 3C(s) + 3O_2(g) \text{ --> } 3CO_2(g) \qquad \Delta H_2 = 3 \times \Delta H_f^o\,(CO_2(g))$

$+ 4H_2(g) + 2O_2(g) \text{ --> } 4H_2O(l) \qquad \Delta H_3 = 4 \times \Delta H_f^o\,(H_2O\,(l))$

$C_3H_8\,(g) + 5\,O_2\,(g) \text{ --> } 3CO_2\,(g) + 4H_2O(l)$

$$\Delta H^o_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Looking up the standard heats of formation for each equation

$\Delta H^o_{rxn} = -(-103.85) + 3(-393.5) + 4(-285.8)) = -2220 \text{ kJ}$

In general,

$\Delta H^o_{rxn} = \Sigma\, n\, \Delta H_f^o\,(\text{products}) - \Sigma\, n\, \Delta H_f^o\,(\text{reactants})$

n is the stoichiometric coefficients in the reaction

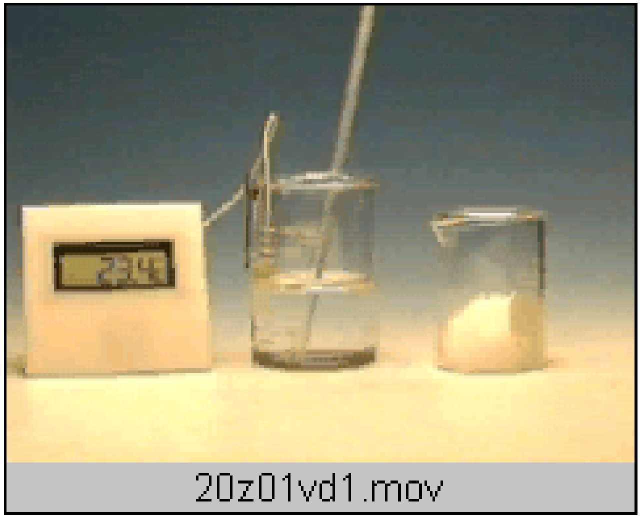
Spontaneous Reactions

In general, spontaneous reactions are exothermic.

$Fe_2O_3(s) + 2Al(s) \rightarrow 2\,Fe(s) + Al_2O_3(s)$

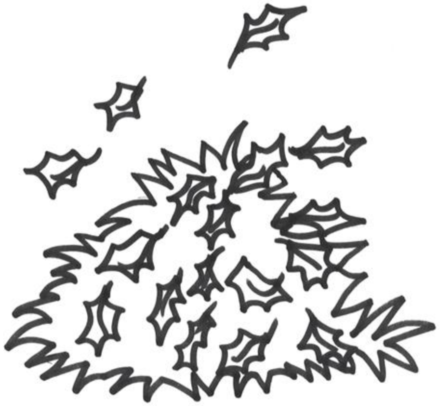
$\Delta H = -848\ kJ$

But many spontaneous reactions or processes are endothermic or even have $\Delta H = 0$.



$NH_4NO_3(s) + heat \rightarrow NH_4NO_3(aq)$

Entropy increases in nature



Temperature differences between systems in contact with each other tend to even out and that work can be obtained from these non-equilibrium differences, but that loss of heat occurs, in the form of entropy, when work is done

- In a system, a process that occurs will tend to increase the total entropy of the universe
- Heat generally cannot flow spontaneously from a material at lower temperature to a material at higher temperature (Clausius)
- It is impossible to convert heat completely into work in a cyclic process (Kelvin)

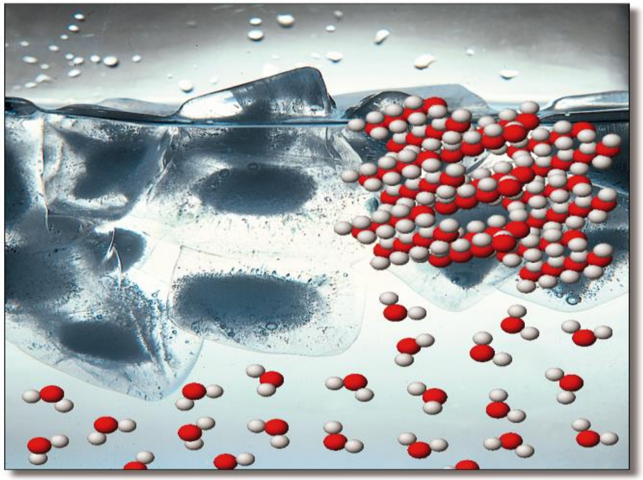
Entropy, S

One property common to spontaneous processes is that the final state is more DISORDERED or RANDOM than the original.

Spontaneity is related to an increase in randomness.

The thermodynamic property related to randomness is ENTROPY, S.

Reaction of K with water

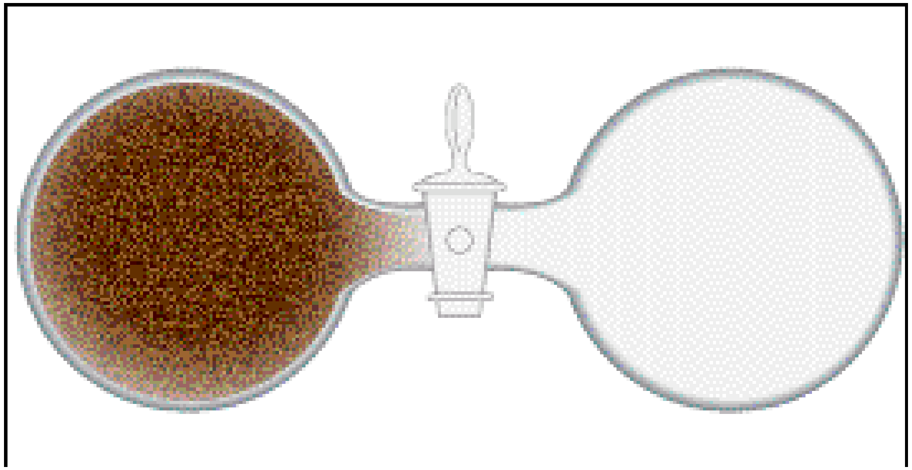


The entropy of liquid water is greater than the entropy of solid water (ice) at 0˚ C.

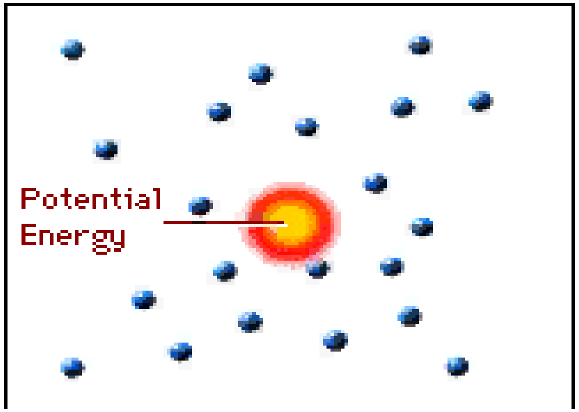
Directionality of Reactions

Probability suggests that a spontaneous reaction will result in the dispersal of energy or of matter or both.

Matter Dispersal



Energy Dispersal



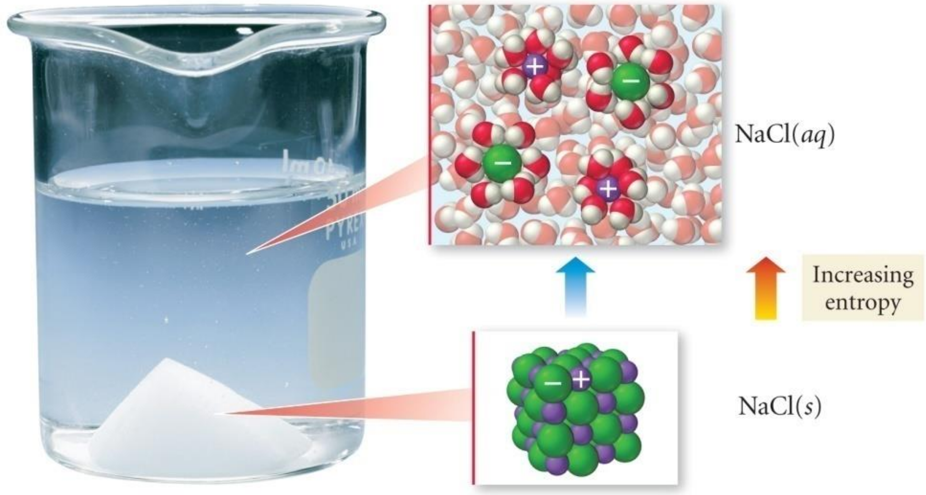
Entropy

The total entropy of the universe increases whenever an irreversible process occurs.

- **The total entropy of the universe is unchanged whenever a reversible process occurs.**

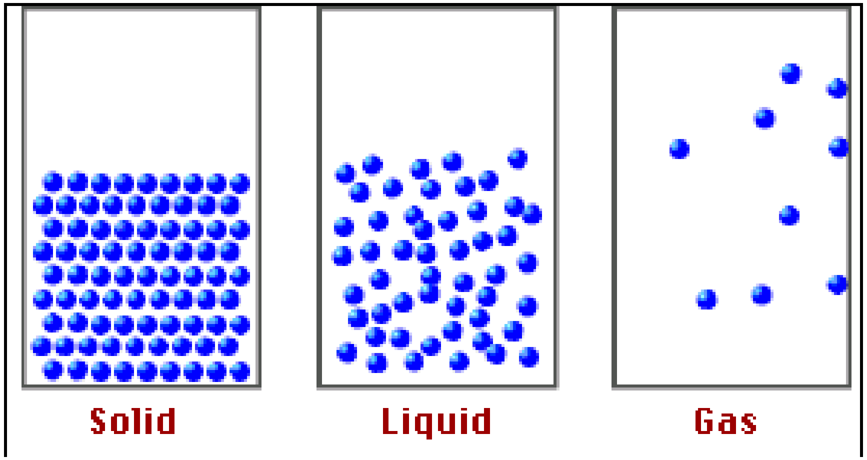
Since all real processes are irreversible, the entropy of the universe continually increases. If entropy decreases in a system due to work being done on it, a greater increase in entropy occurs outside the system.

Entropy, S



Entropy (S) = driving force of spontaneous reactions = disorder or random

Entropy of a substance increases with temperature.

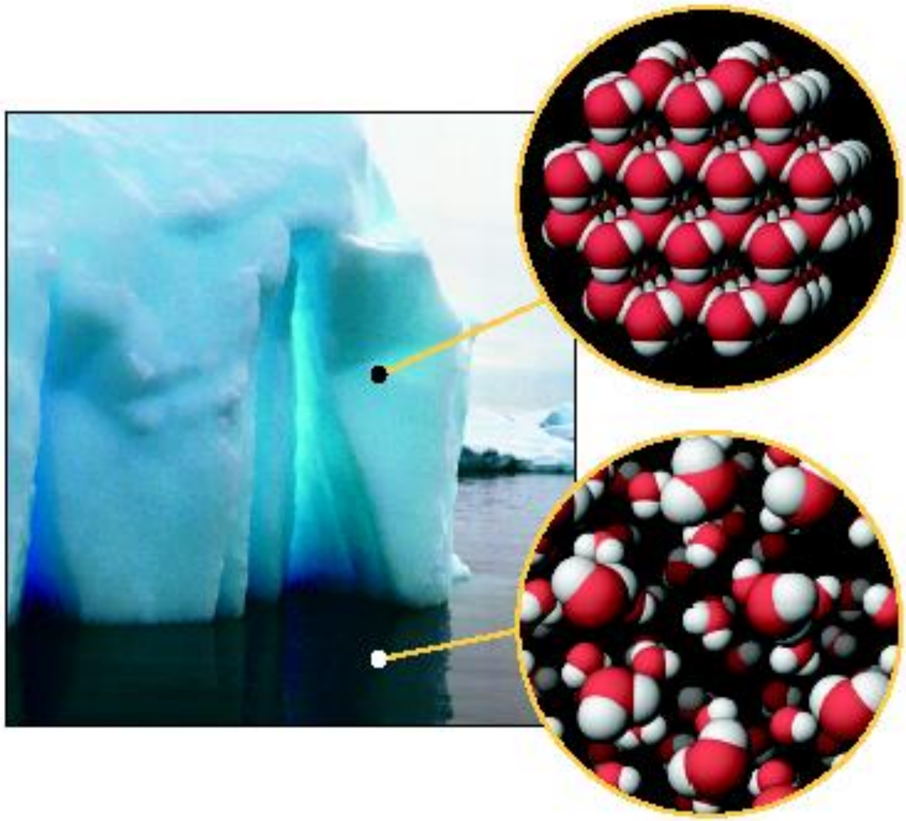


	S° (J/K•mol)
H_2O(liq)	69.95
H_2O(gas)	188.8

S (gases) > S (liquids) > S (solids)

Entropy and States of Matter

$S^\circ(\mathrm{Br_2\ liq}) < S^\circ(\mathrm{Br_2\ gas})$

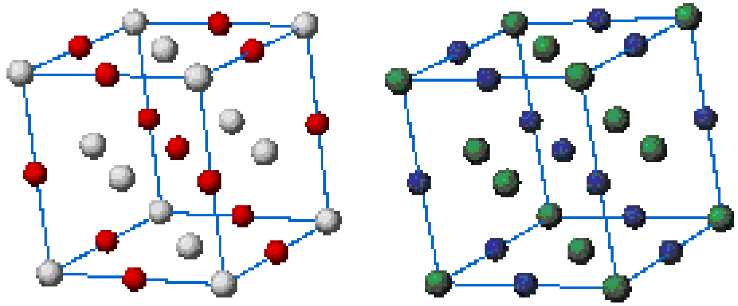


$S^\circ(\mathrm{H_2O\ sol}) < S^\circ(\mathrm{H_2O\ liq})$

Entropy, S

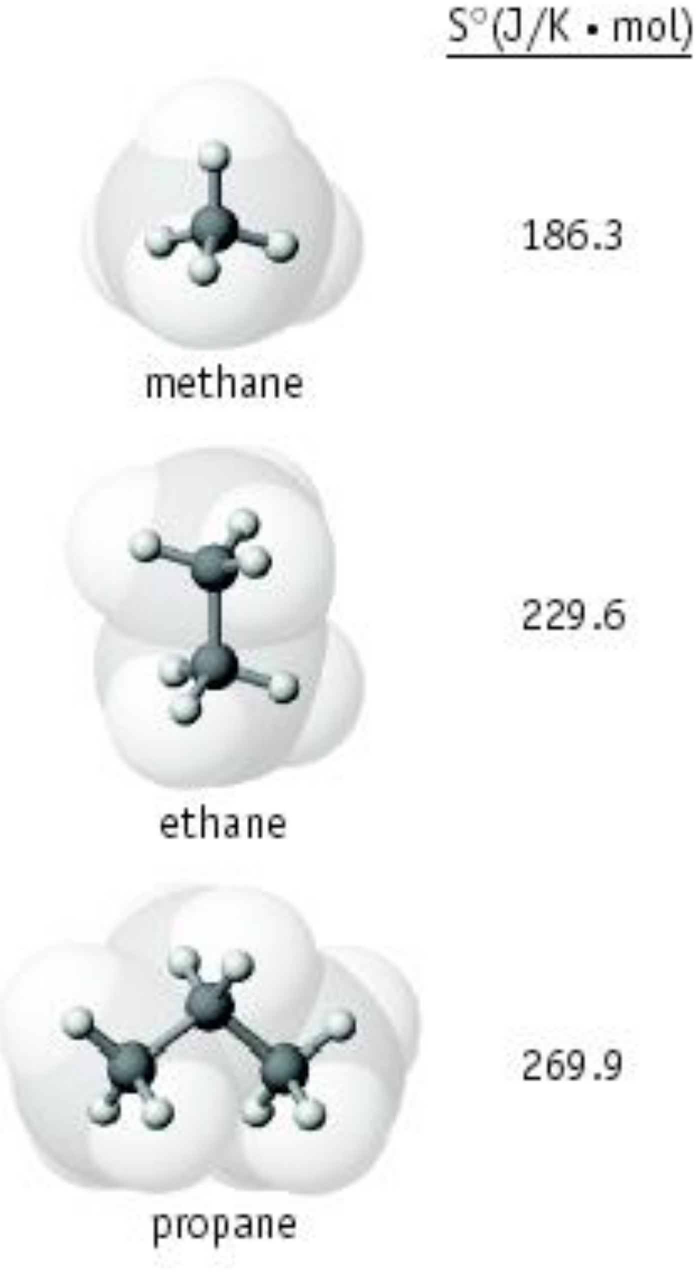
Increase in molecular complexity generally leads to increase in S.

Entropies of ionic solids depend on coulombic attractions.

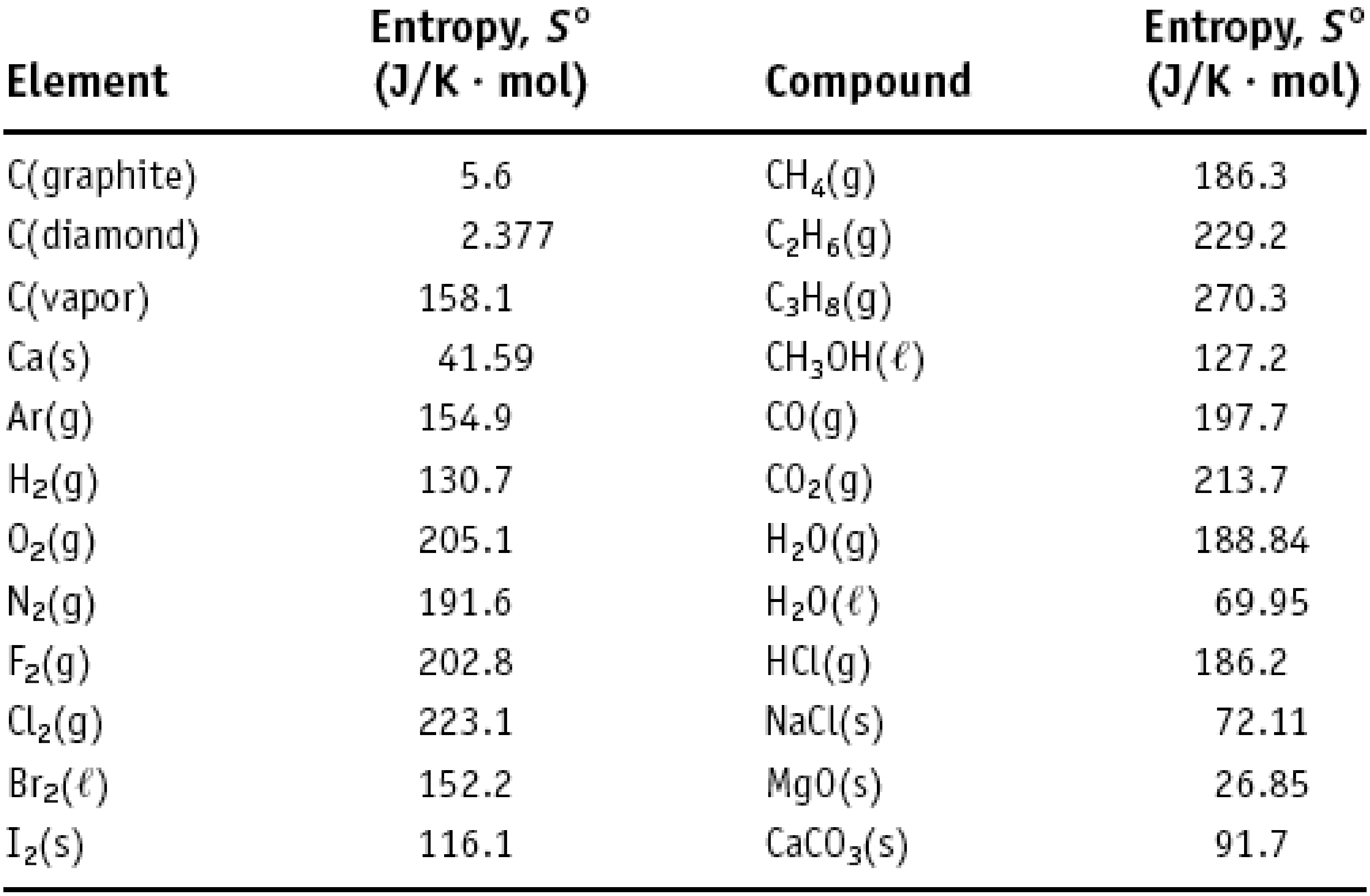

Magnesium Oxide

Sodium Fluoride

S^o (J/K•mol)	
MgO	26.9
NaF	51.5

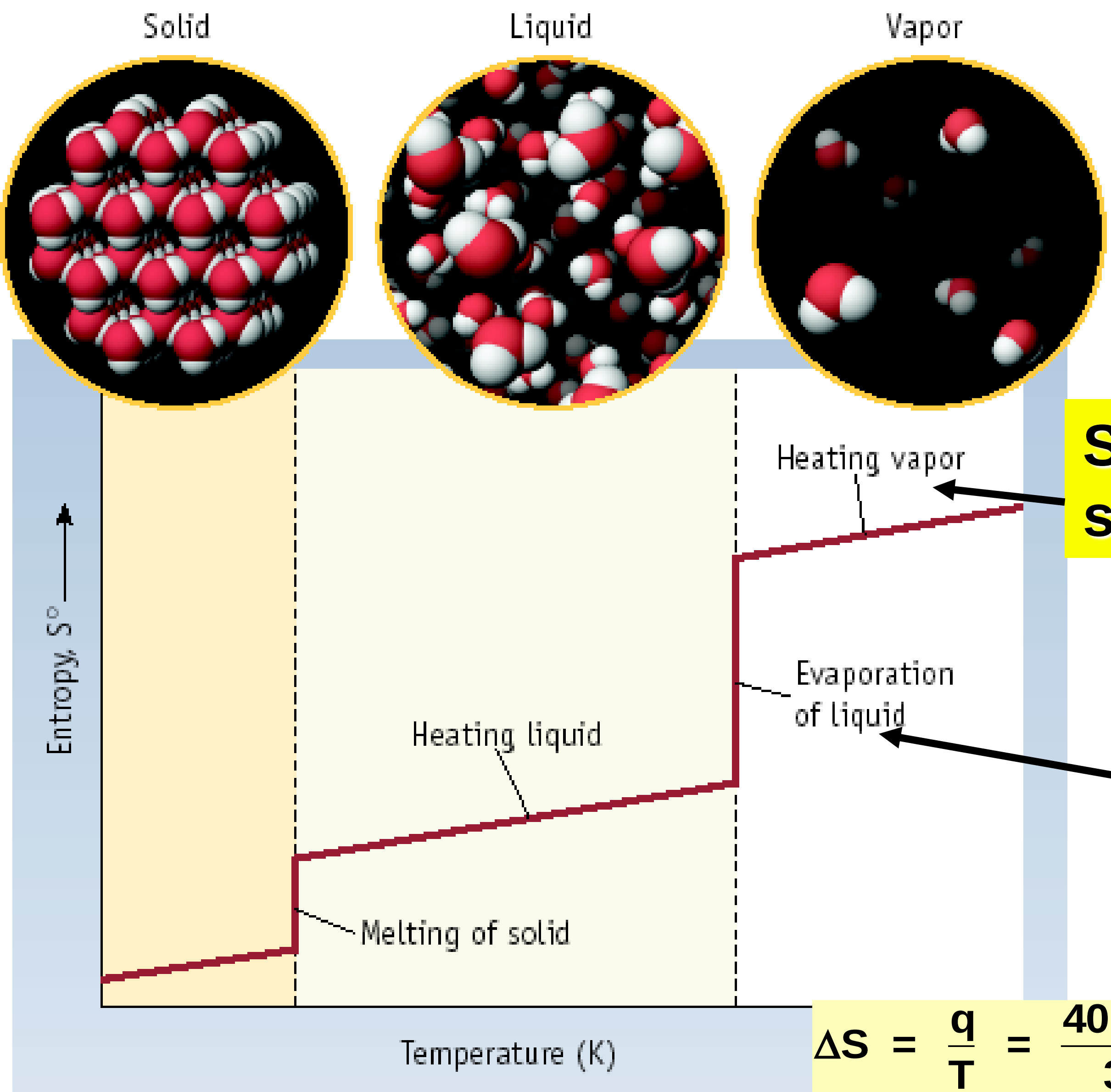


Some Standard Molar Entropies at 298 K



Element	Entropy, $S°$ (J/K · mol)	Compound	Entropy, $S°$ (J/K · mol)
C(graphite)	5.6	$CH_4(g)$	186.3
C(diamond)	2.377	$C_2H_6(g)$	229.2
C(vapor)	158.1	$C_3H_8(g)$	270.3
Ca(s)	41.59	$CH_3OH(\ell)$	127.2
Ar(g)	154.9	CO(g)	197.7
$H_2(g)$	130.7	$CO_2(g)$	213.7
$O_2(g)$	205.1	$H_2O(g)$	188.84
$N_2(g)$	191.6	$H_2O(\ell)$	69.95
$F_2(g)$	202.8	HCl(g)	186.2
$Cl_2(g)$	223.1	NaCl(s)	72.11
$Br_2(\ell)$	152.2	MgO(s)	26.85
$I_2(s)$	116.1	$CaCO_3(s)$	91.7

Temperature and phase change influence



For a phase change,

$\Delta S = q/T$

where q = heat transferred in phase change

For H_2O (liq) ---> $H_2O(g)$

$\Delta H = q = +40{,}700$ J/mol

S increases slightly with T

S increases a large amount with phase changes

$$\Delta S = \frac{q}{T} = \frac{40{,}700\ \text{J/mol}}{373.15\ \text{K}} = +109\ \text{J/K} \cdot \text{mol}$$

Calculating ΔS for a Reaction

$$\Delta S^o = \Sigma S^o \text{ (products)} - \Sigma S^o \text{ (reactants)}$$

Consider $2 H_2(g) + O_2(g) \text{ ---> } 2 H_2O(liq)$

$\Delta S^o = 2 S^o (H_2O) - [2 S^o (H_2) + S^o (O_2)]$

ΔS^o = 2 mol (69.9 J/K•mol) - [2 mol (130.7 J/K•mol) + 1 mol (205.3 J/K•mol)]

ΔS^o = -326.9 J/K

Note that there is a decrease in S because 3 mol of gas give 2 mol of liquid.

2nd Law of Thermodynamics

A reaction is spontaneous if ΔS for the universe is positive.

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

$\Delta S_{universe} > 0$ for spontaneous process

Life = constant battle against entropy

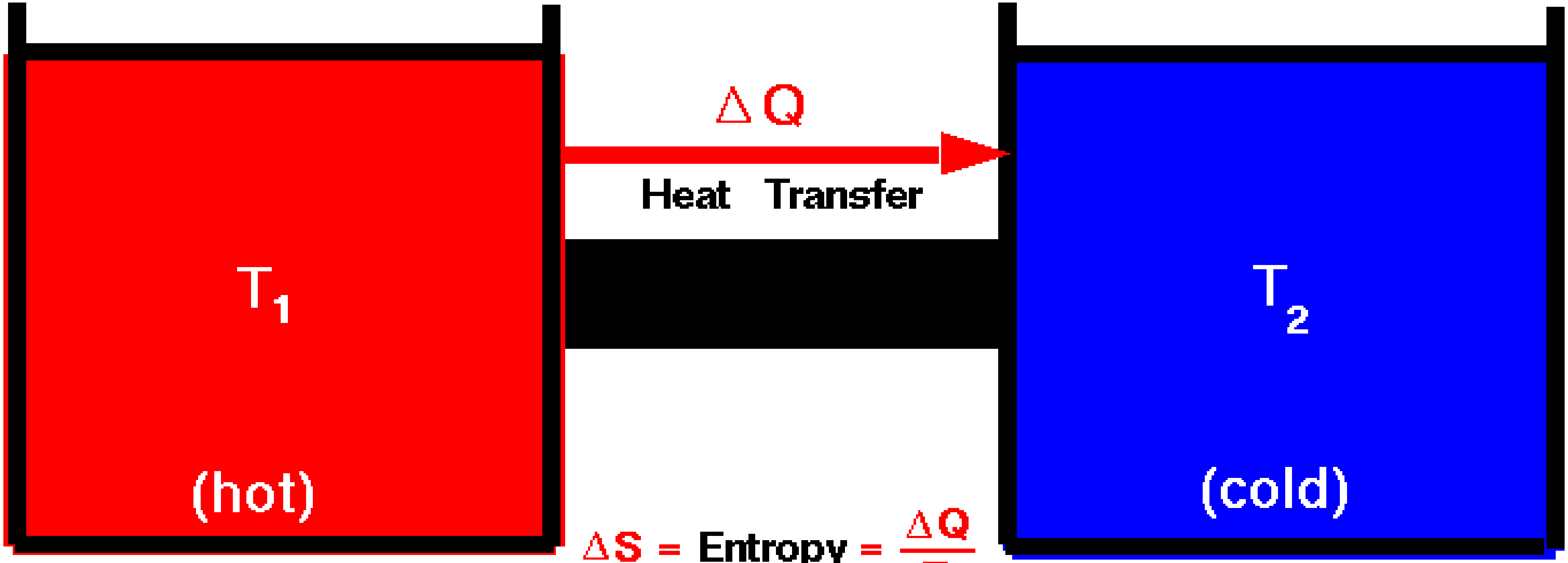
Large molecules are assembled from smaller ones.

Organizing a cell is ΔS_{system} = - the process is not spontaneous

Fortunately, it is $\Delta S_{universe}$ that must be positive in a process Surroundings = large + for life to occur

Second Law of Thermodynamics

Glenn
Research
Center



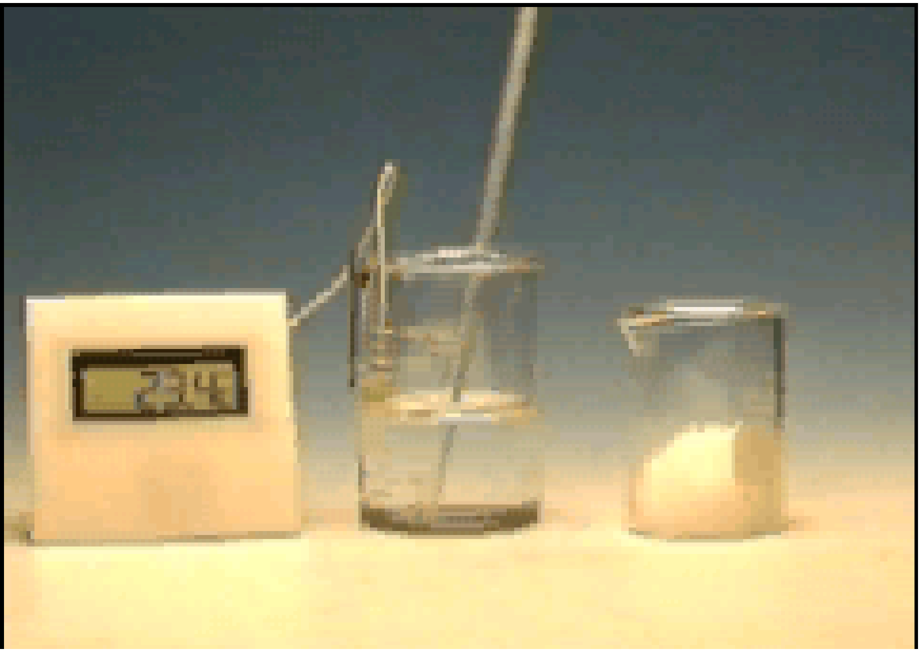
$$\Delta S = \text{Entropy} = \frac{\Delta Q}{T}$$

There exists a useful thermodynamic variable called entropy (S). A natural process that starts in one equilibrium state and ends in another will go in the direction that causes the entropy of the system plus the environment to increase for an irreversible process and to remain constant for a reversible process.

$S_f = S_i$ (reversible)

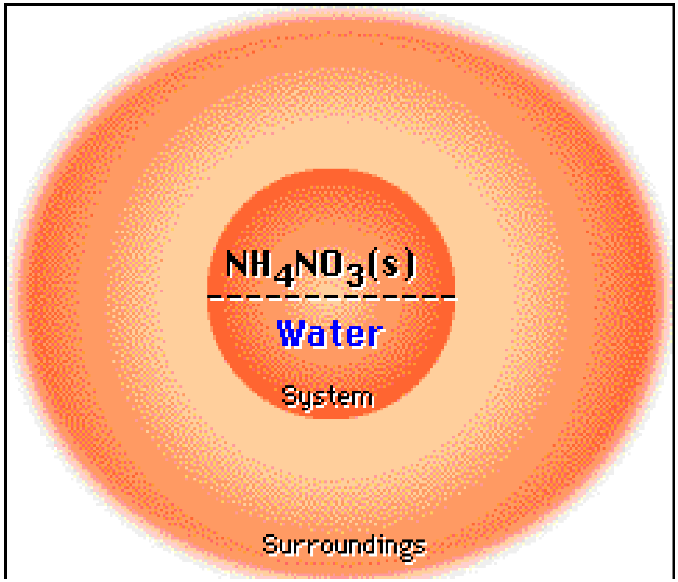
$S_f > S_i$ (irreversible)

2nd Law of Thermodynamics



Dissolving NH_4NO_3 in water—an entropy driven process.

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$



2nd Law of Thermodynamics

$2\ H_2(g) + O_2(g) \text{ ---> } 2\ H_2O(liq)$

$\Delta S^o_{system} = -326.9 \text{ J/K}$

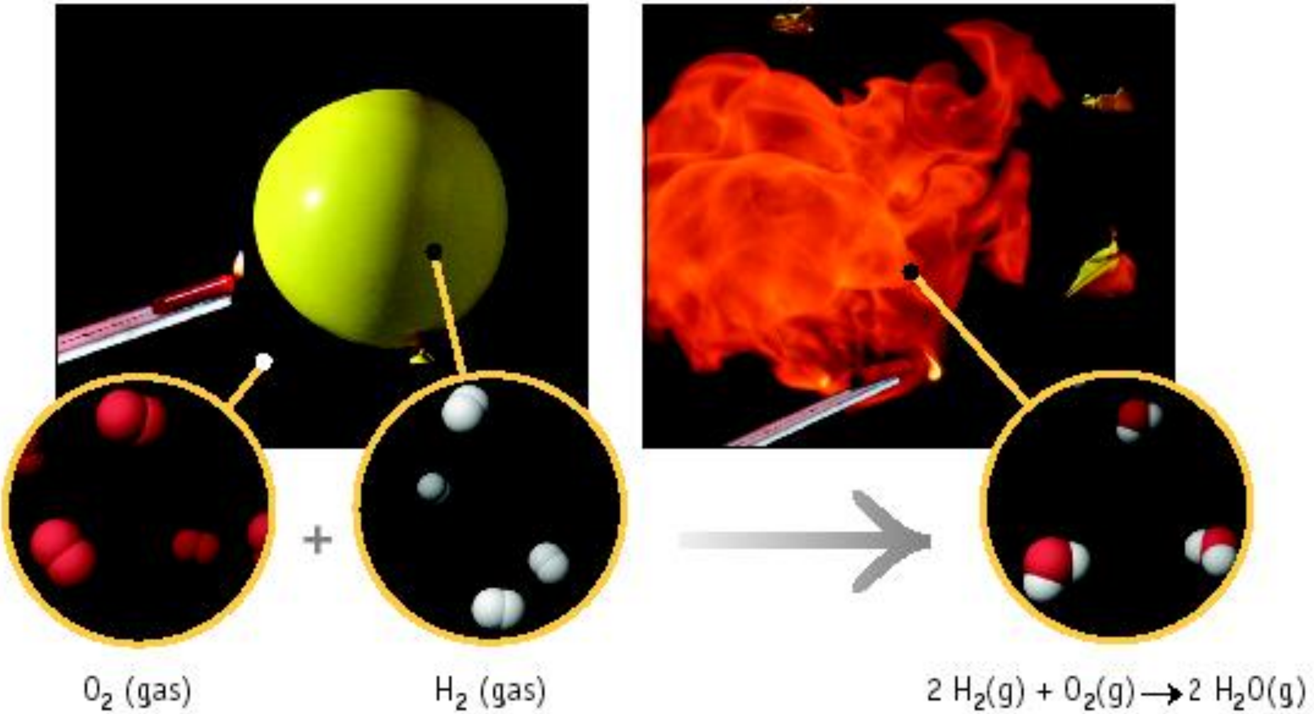
$$\Delta S^o_{surroundings} = \frac{q_{surroundings}}{T} = \frac{-\Delta H_{system}}{T}$$

Can calc. that $\Delta H^o_{rxn} = \Delta H^o_{system} = -571.7$ kJ

$$\Delta S^o_{surroundings} = \frac{-(-571.7 \text{ kJ})(1000 \text{ J/kJ})}{298.15 \text{ K}}$$

$\Delta S^o_{surroundings} = +1917 \text{ J/K}$

2nd Law of Thermodynamics



$2\ H_2(g) + O_2(g) \text{ ---> } 2\ H_2O(liq)$

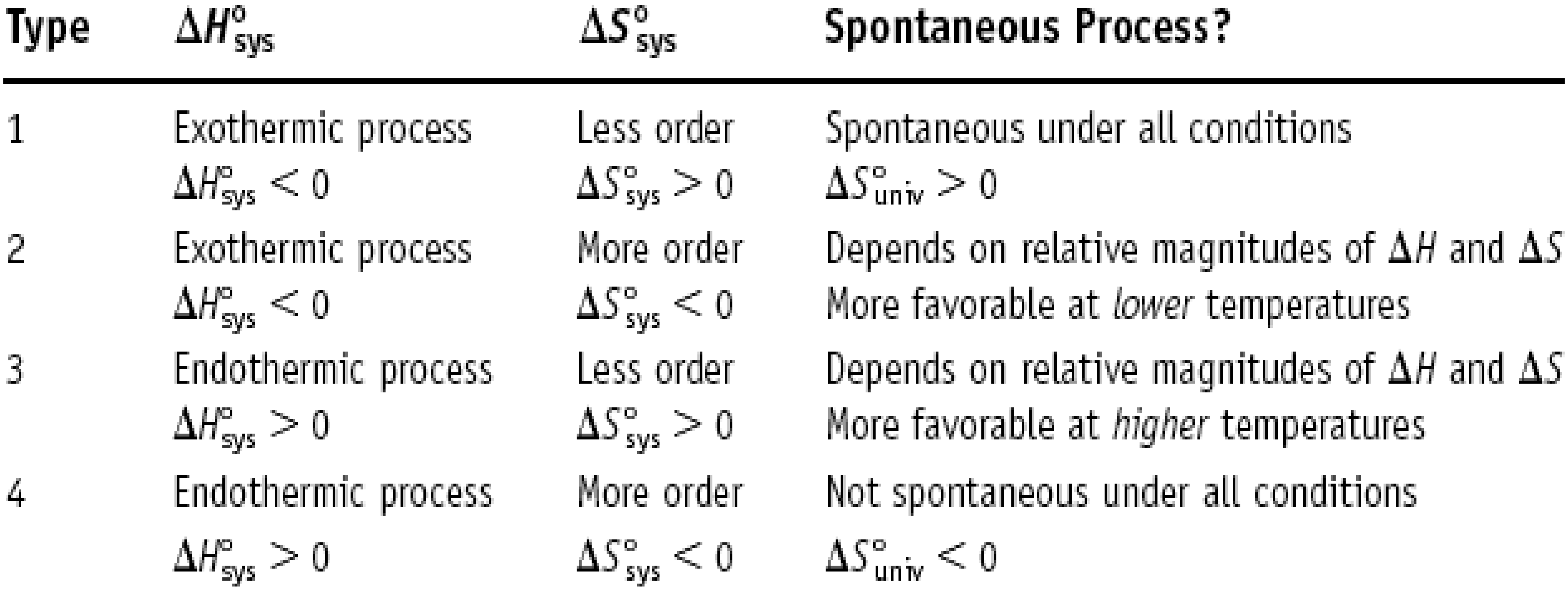
$\Delta S^o_{system} = -326.9$ J/K

$\Delta S^o_{surroundings} = +1917$ J/K

$\Delta S^o_{universe} = +1590.$ J/K

- ***The entropy of the universe is increasing, so the reaction is product-favored.***

Spontaneous or Not?



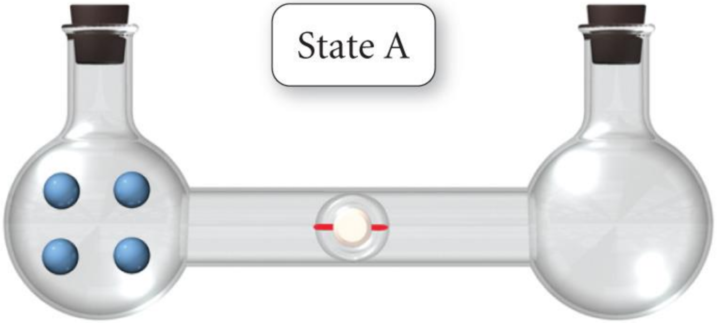
Type	ΔH°_{sys}	ΔS°_{sys}	Spontaneous Process?
1	Exothermic process $\Delta H^\circ_{sys} < 0$	Less order $\Delta S^\circ_{sys} > 0$	Spontaneous under all conditions $\Delta S^\circ_{univ} > 0$
2	Exothermic process $\Delta H^\circ_{sys} < 0$	More order $\Delta S^\circ_{sys} < 0$	Depends on relative magnitudes of ΔH and ΔS More favorable at *lower* temperatures
3	Endothermic process $\Delta H^\circ_{sys} > 0$	Less order $\Delta S^\circ_{sys} > 0$	Depends on relative magnitudes of ΔH and ΔS More favorable at *higher* temperatures
4	Endothermic process $\Delta H^\circ_{sys} > 0$	More order $\Delta S^\circ_{sys} < 0$	Not spontaneous under all conditions $\Delta S^\circ_{univ} < 0$

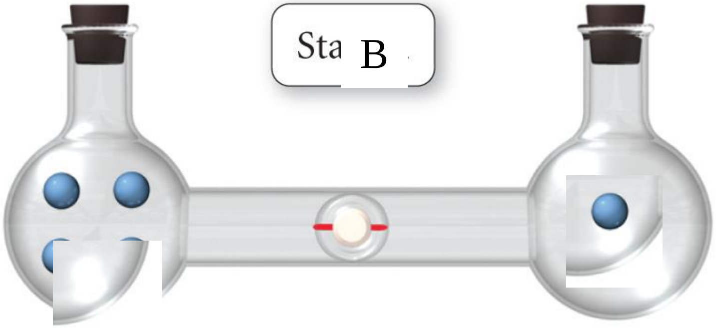
Remember that $-\Delta H^\circ_{sys}$ is proportional to ΔS°_{surr}

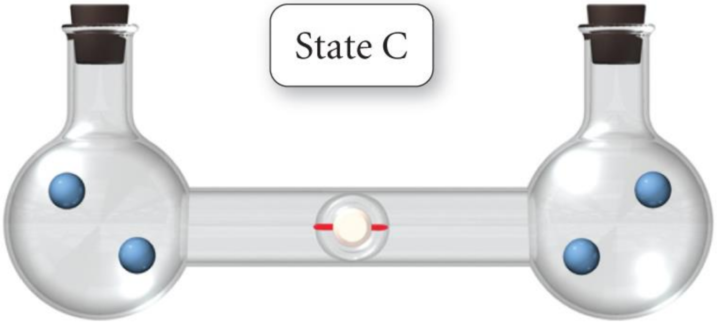
An exothermic process has $\Delta S^\circ_{surr} > 0$.

Possible arrangements of 4 gas molecules in a 2-bulb system

Microstates = possible configurations of a particular arrangement







Microstates		Order
ABCD	---	1 microstate Ordered
ABC	D	4 microstates Somewhat Disordered
ABD	C	
ACD	B	
BCD	A	
AB	CD	6 microstates Fully disordered
CD	AB	
AC	BD	
BD	AC	
AD	BC	
BC	AD	

Entropy selects most likely arrangement = 2 molecules in each bulb

Free Energy (*G*)

- Gibbs Free Energy is the total energy (both H and S) that is available to do work
- A process (at constant *T* and *P*) is spontaneous in the direction in which the free energy decreases.
- Negative ΔG means positive ΔS_{univ}.

$$\Delta G = \Delta H - T\Delta S \text{ (at constant } T \text{ and } P\text{)}$$

- The change in free energy that will occur if the reactants in their standard states are converted to the products in their standard states.

$$\Delta G^\circ_{\text{reaction}} = \Sigma G^\circ_{\text{products}} - \Sigma G^\circ_{\text{reactants}}$$

Free Energy (Gibbs energy)

Free Energy $\Delta G_{process} = \Delta H - T\Delta S$

$$\Delta S_{univ} = -\frac{\Delta G}{T}$$

1) A process is spontaneous if $\Delta G = <0$
2) Chemists use ΔG rather than ΔS because we only need to know system

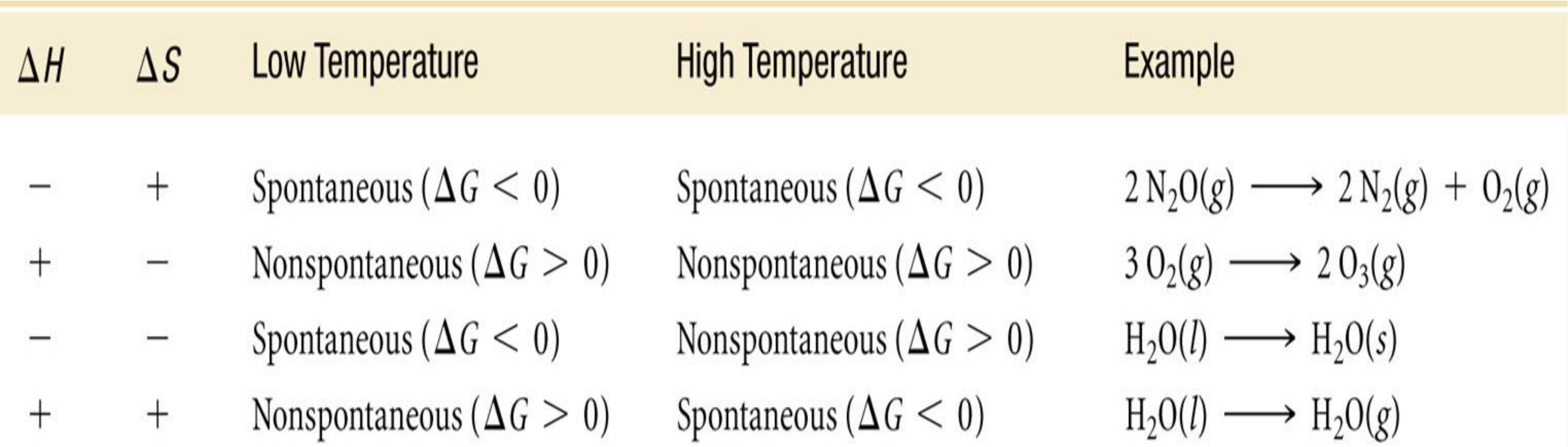
$$-\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S = \Delta S_{surr} + \Delta S = \Delta S_{univ}$$

Example: Predicting Spontaneity using ΔG

$H_2O(s) \longrightarrow H_2O(l)$ $\Delta H^o = 6030$ J/mol, $\Delta S^o = 22.1$ J/K mol

T	T	ΔH^o	ΔS^o	ΔS_{surr}	ΔS_{univ}	$T\Delta S^o$	ΔG^o
^oC	K	J/mol	J/K•mol	J/K•mol	J/K • mol	J/mol	J/mol
-10	263	6030	22.1	-22.9	-0.8	5810	+220
0	273	6030	22.1	-22.1	0.0	6030	0
10	283	6030	22.1	-21.3	0.8	6250	-220

Classifying Processes/Reactions based on ΔH and ΔS



ΔH	ΔS	Low Temperature	High Temperature	Example
$-$	$+$	Spontaneous ($\Delta G < 0$)	Spontaneous ($\Delta G < 0$)	$2\,N_2O(g) \longrightarrow 2\,N_2(g) + O_2(g)$
$+$	$-$	Nonspontaneous ($\Delta G > 0$)	Nonspontaneous ($\Delta G > 0$)	$3\,O_2(g) \longrightarrow 2\,O_3(g)$
$-$	$-$	Spontaneous ($\Delta G < 0$)	Nonspontaneous ($\Delta G > 0$)	$H_2O(l) \longrightarrow H_2O(s)$
$+$	$+$	Nonspontaneous ($\Delta G > 0$)	Spontaneous ($\Delta G < 0$)	$H_2O(l) \longrightarrow H_2O(g)$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

$$\Delta G = 0 = \Delta G^\circ + RT \ln(K)$$

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

Signs of Thermodynamic Values

	Negative	Positive
Enthalpy (ΔH)	Exothermic	Endothermic
Entropy (ΔS)	Less disorder	More disorder
Gibbs Free Energy (ΔG)	Spontaneous	Not spontaneous

3rd Law of Thermodynamic

The entropy of a perfect crystal at 0 K is zero. The entropy of a substance increases with temperature.

- No system can reach absolute zero
- This is one reason we use the Kelvin temperature scale. Not only is the internal energy proportional to temperature, but you never have to worry about dividing by zero in an equation!
- There is no formula associated with the 3rd Law of Thermodynamics

Chemical Kinetics

Chemical kinetics: the study of *reaction rate*, ← a quantity conditions affecting it, the molecular events during a chemical reaction (mechanism), and presence of other components (catalysis).

Factors affecting reaction rate:

Concentrations of reactants
Catalyst
Temperature
Surface area of solid reactants or catalyst

Chemical Kinetics

Thermodynamics – does a reaction take place?

Kinetics – how fast does a reaction proceed?

Reaction rate is the change in the concentration of a reactant or a product with time (*M*/s).

$$A \longrightarrow B$$

$$\text{rate} = \enclose{circle}{-}\,\frac{\Delta[A]}{\Delta t}$$

$\Delta[A]$ = change in concentration of A over time period Δt

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

$\Delta[B]$ = change in concentration of B over time period Δt

Because [A] decreases with time, $\Delta[A]$ is negative.

Factors that Affect Reaction Rate

1. **Temperature**
   - **Collision Theory:** When two chemicals react, their molecules have to collide with each other with sufficient energy for the reaction to take place.
   - **Kinetic Theory:** Increasing temperature means the molecules move faster.
2. **Concentrations of reactants**

   More reactants mean more collisions if enough energy is present
3. **Catalysts**

   Speed up reactions by lowering activation energy
4. **Surface area of a solid reactant**

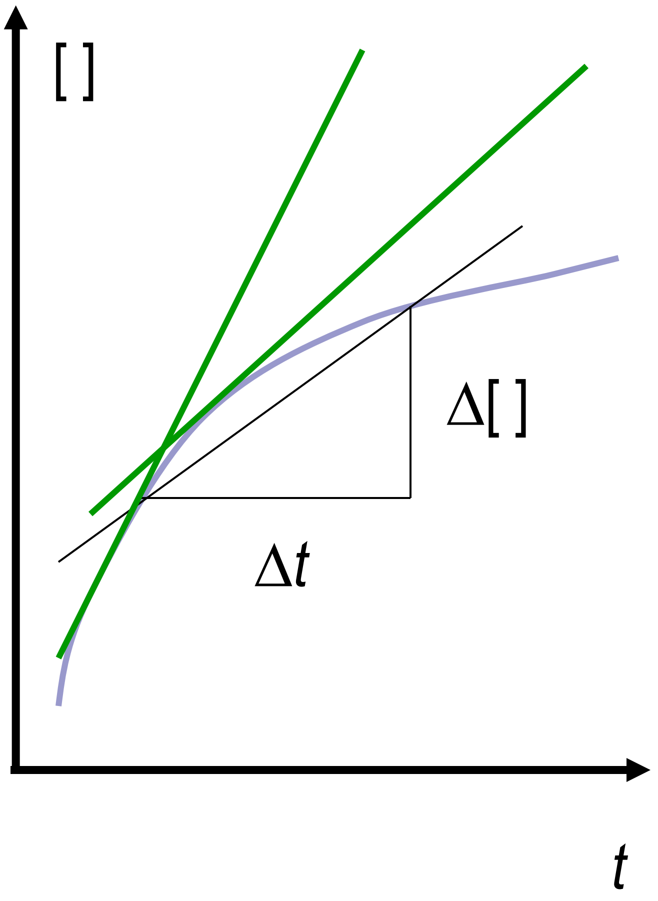
   Bread and Butter theory: more area for reactants to be in contact
5. **Pressure of gaseous reactants or products**

   Increased number of collisions

Reaction Rate Defined

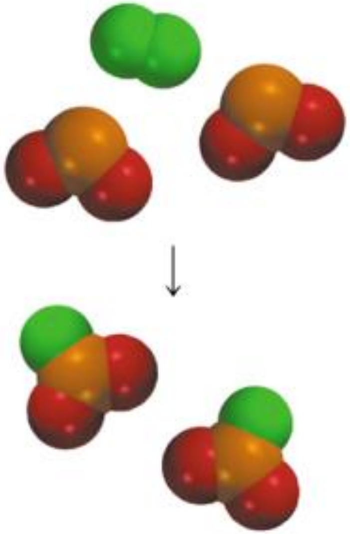
Reaction rate: changes in a concentration of a product or a reactant per unit time.

$$\textit{Reaction rate} = \frac{\Delta\boxed{[\ ]} \longrightarrow \text{concentration}}{\underset{\hookrightarrow \text{change}}{\Delta}\, t}$$



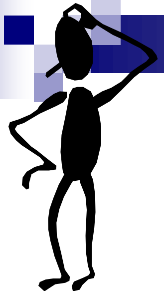
Rate Laws

- Rate laws are **always** determined experimentally.
- Reaction order is **always** defined in terms of reactant (not product) concentrations.
- The order of a reactant **is not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation.



$$F_2\,(g) + \boxed{2}ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$$

$$\text{rate} = k\,[F_2][ClO_2]^{\boxed{1}}$$



Determine the rate law and calculate the rate constant for the following reaction from the following data:

$S_2O_8^{2-}\ (aq) + 3I^-\ (aq) \longrightarrow 2SO_4^{2-}\ (aq) + I_3^-\ (aq)$

Experiment	$[S_2O_8^{2-}]$	$[I^-]$	Initial Rate (M/s)
1	0.08	0.034	2.2×10^{-4}
2	0.08	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

rate = $k\,[S_2O_8^{2-}]^x[I^-]^y$

$y = 1$

$x = 1$

rate = $k\,[S_2O_8^{2-}][I^-]$

Double $[I^-]$, rate doubles (experiment 1 & 2)

Double $[S_2O_8^{2-}]$, rate doubles (experiment 2 & 3)

$$k = \frac{\text{rate}}{[S_2O_8^{2-}][I^-]} = \frac{2.2 \times 10^{-4}\ M/\text{s}}{(0.08\ M)(0.034\ M)} = 0.08/M\bullet\text{s}$$

Differential Rate Laws

Dependence of reaction rate on the concentrations of reactants is called the rate law, which is unique for each reaction.

For a general reaction, $a\,A + b\,B + c\,C \rightarrow \textit{products}$

the rate law has the general form

order wrt *A*, *B*, and *C*, determined experimentally

$$\textit{reaction rate} = k\,[A]^{x}[B]^{y}[C]^{z}$$

the rate constant

For example, the rate law is

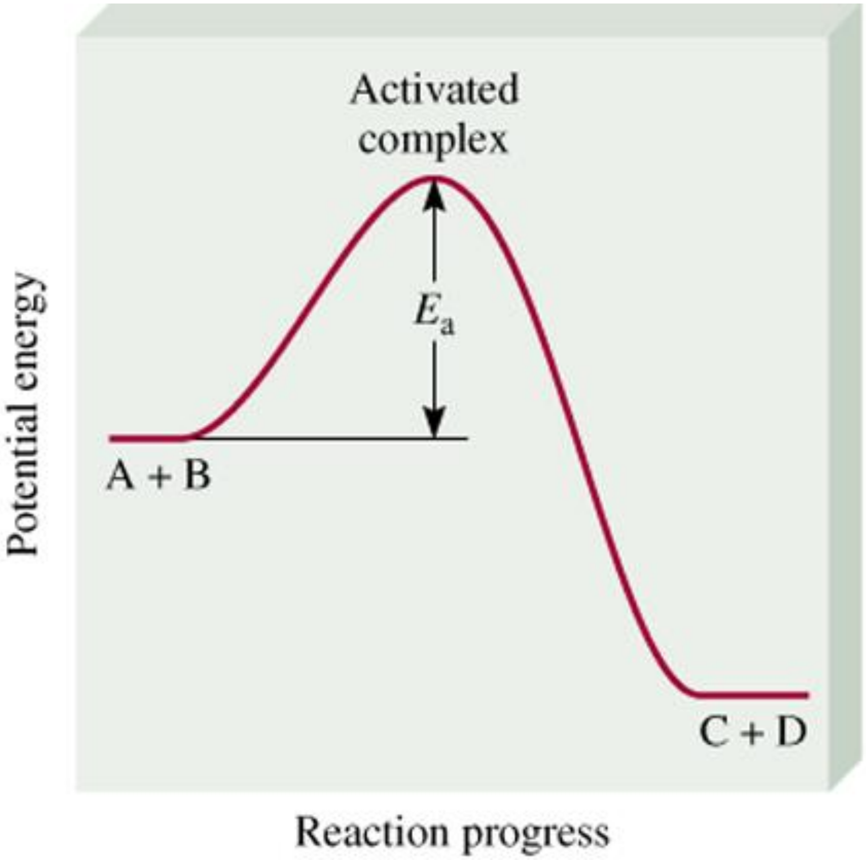
$rate = k\,[Br^-]\,[BrO_3^-]\,[H^+]$ for

$5\,Br^- + BrO_3^- + 6\,H^+ \rightarrow 3Br_2 + 3\,H_2O$

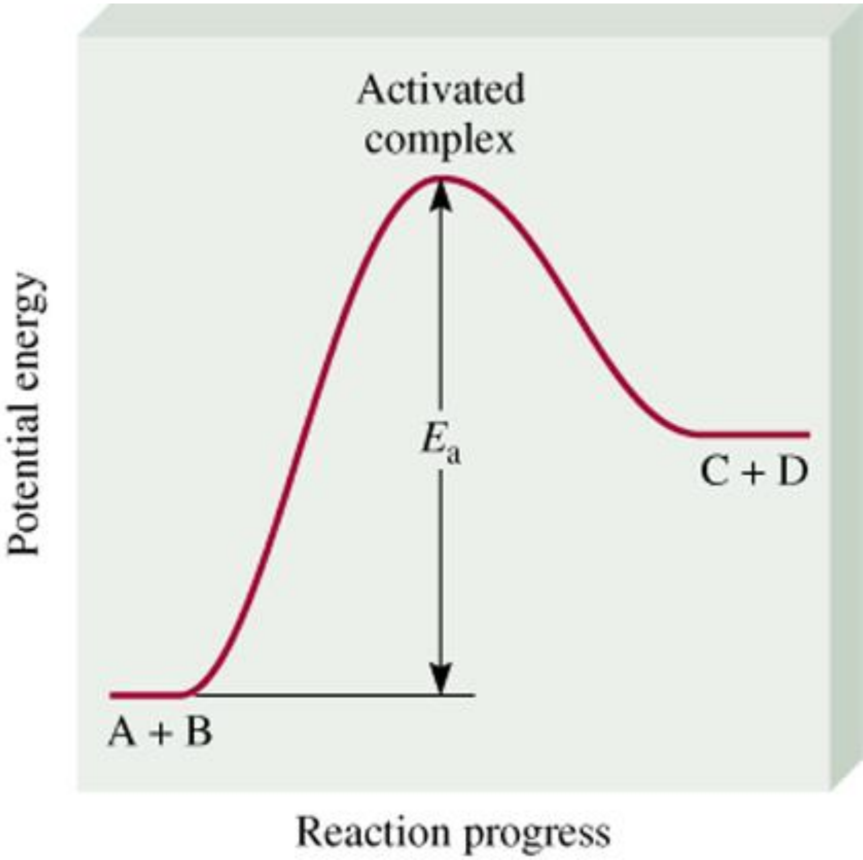
Use differentials to express rates

The reaction is 1st order with all three reactants, total order 3.

Exothermic Reaction



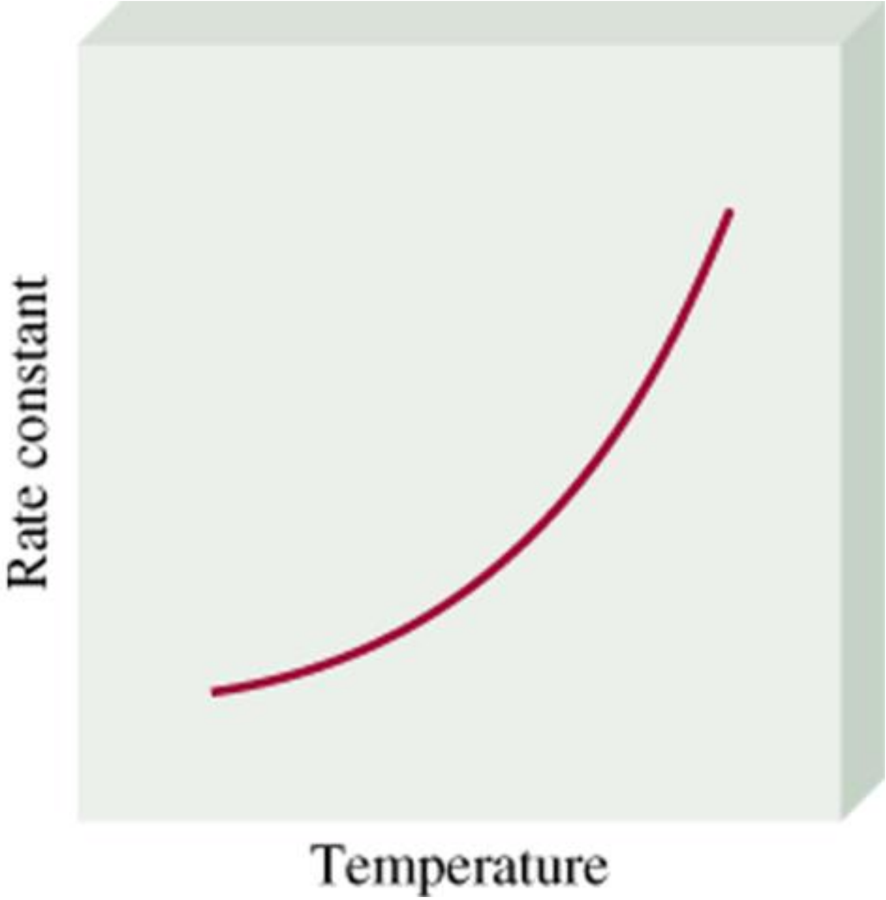
Endothermic Reaction



The ***activation energy (E_a)*** is the minimum amount of energy required to initiate a chemical reaction.

$$A + B \longrightarrow C + D$$

Temperature Dependence of the Rate Constant



$k = A \cdot \exp(-E_a/RT)$

(Arrhenius equation)

E_a is the activation energy (J/mol)

R is the gas constant (8.314 J/K•mol)

T is the absolute temperature

A is the frequency factor

$$\boxed{\ln k = \frac{-E_a}{R} \frac{1}{T} + \ln A}$$

Chemical Reaction and Molecular Collision

Molecular collisions lead to chemical reactions. Thus, the reaction constant, *k* is determined by several factors.

$$k = Z f p$$

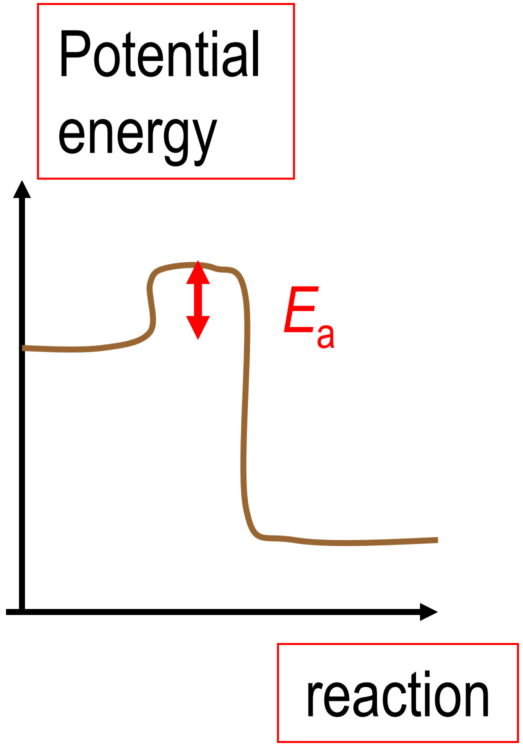
Z: collision frequency

p, the fraction with proper orientation

constant

f, fraction of collision having sufficient energy for reaction

f is related to the potential energy barrier called activation energy, E_a.



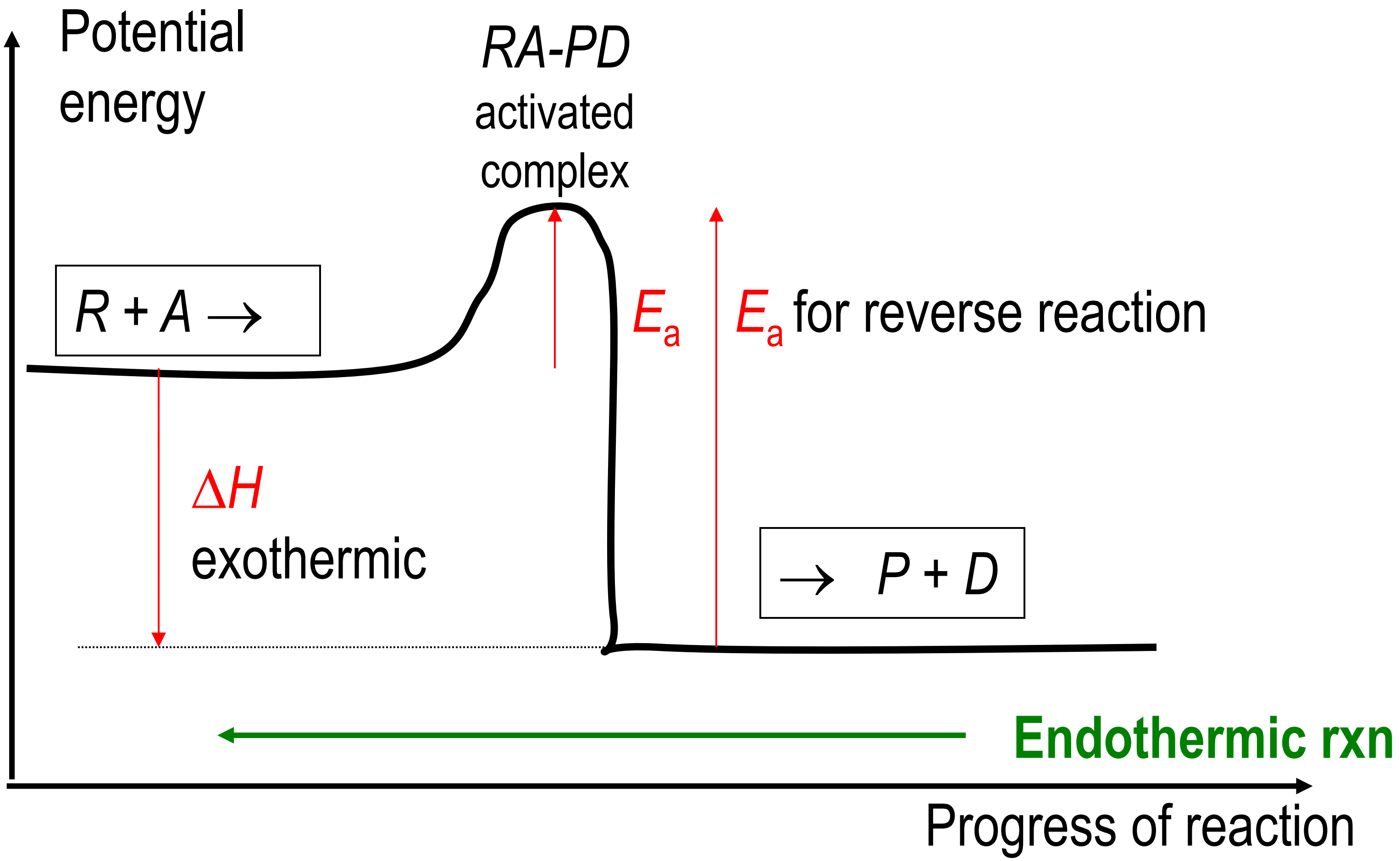
$$f \infty e^{-Ea/RT} \text{ or } \exp(-E_a / R\,T)$$

Thus, $$k = \underbrace{A}_{\text{constant}} e^{-Ea/RT}$$

How does temperature affect *reaction rates*?

Explain energy aspect in a chemical reaction

Energy in chemical reactions



The Arrhenius Equation

The temperature dependence of the rate constant *k* is best described by the Arrhenius equation:

$$k = A\, e^{-Ea/RT}$$

or $\ln k = \ln A - E_a / R\, T$

If k_1 and k_2 are the rate constants at T_1 and T_2 respectively, then

$$\ln \frac{k_1}{k_2} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

1903 Nobel Prize citation" …in recognition of the extraordinary services he has rendered to the advancement of chemistry by his electrolytic theory of dissociation"

Application of Arrhenius Equation

From $k = A\,e^{-Ea/RT}$, calculate A, E_a, k at a specific temperature and T.

The reaction:

$2\,NO_2(g)$ -----> $2NO(g) + O_2(g)$

The rate constant k = 1.0e-10 s^{-1} at 300 K and the activation energy E_a = 111 kJ mol^{-1}. What are A, k at 273 K and T when k = 1e-11?

Method: derive various versions of the same formula

$$k = A\,e^{-Ea/RT}$$

$$A = k\,e^{Ea/RT}$$

$$A/k = e^{Ea/RT}$$

$$\ln(A/k) = E_a/RT$$

Make sure you know how to transform the formula into these forms.

Catalysis

A catalyst is a substance that changes the *rate of a reaction* by lowing the activation energy, E_a. It participates a reaction in forming an intermediate, but is regenerated.

Enzymes are marvelously selective catalysts.

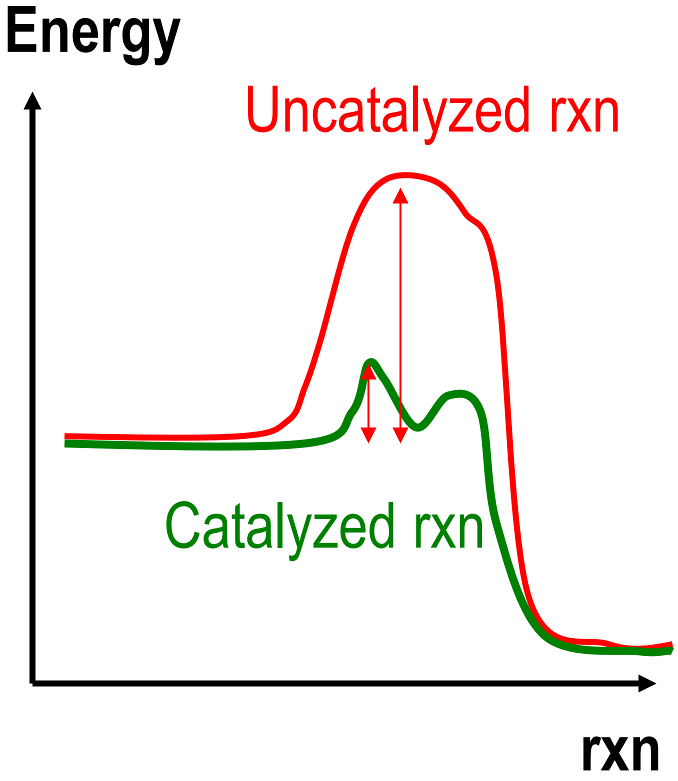
A catalyzed reaction,

$$2\ SO_2\ (g) + O_2 \xrightarrow{\text{NO (catalyst)}} 2\ SO_3\ (g)$$

via the mechanism

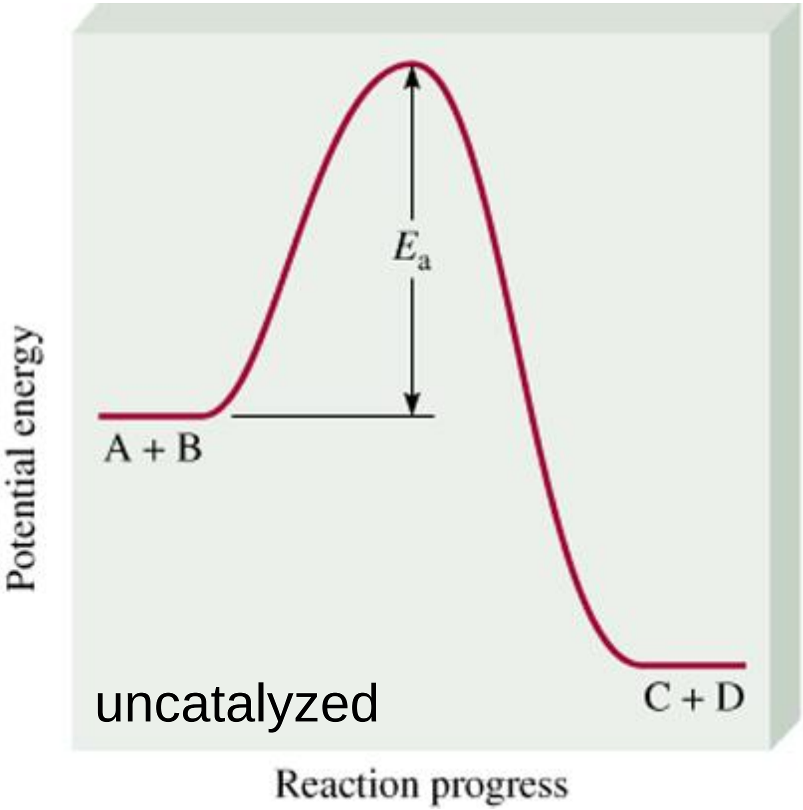
i $2\ NO + O_2 \rightarrow 2\ NO_2$ (3^{rd} order)

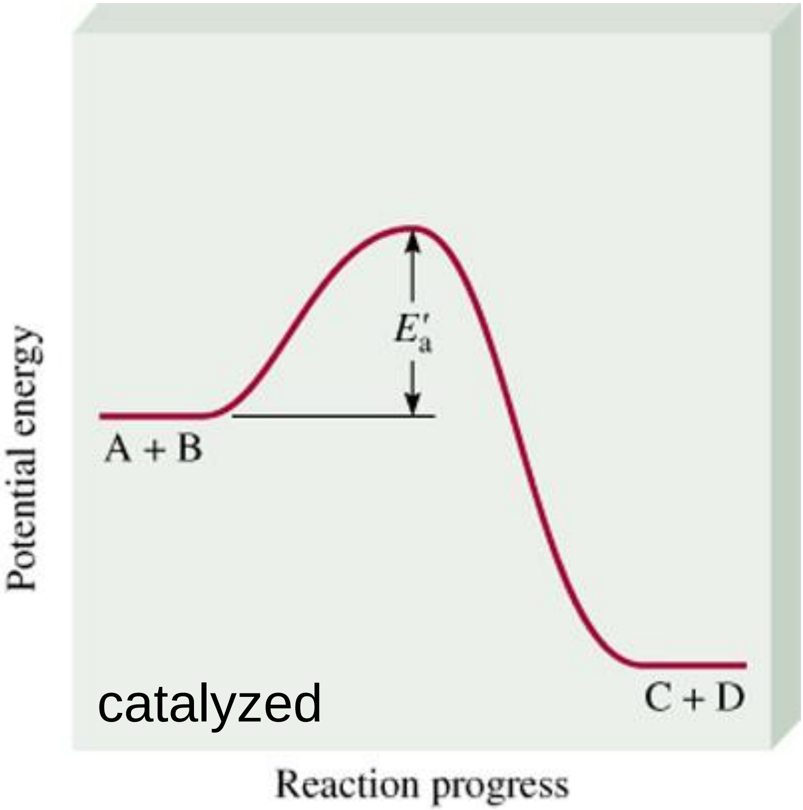
ii $NO_2 + SO_2 \rightarrow SO_3 + NO$



A ***catalyst*** is a substance that increases the rate of a chemical reaction without itself being consumed.

$E_a \downarrow$ $k \uparrow$





$\text{rate}_{\text{catalyzed}} > \text{rate}_{\text{uncatalyzed}}$

Homogenous vs. heterogeneous catalysts

A catalyst in the same phase (gases and solutions) as the reactants is a homogeneous catalyst. It effective, but recovery is difficult.

When the catalyst is in a different phase than reactants (and products), the process involve heterogeneous catalysis. Chemisorption, absorption, and adsorption cause reactions to take place via different pathways.

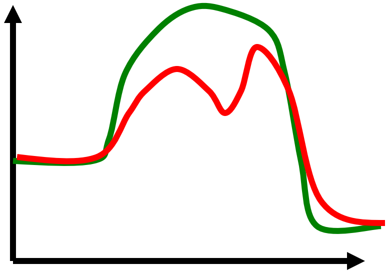
Platinum is often used to catalyze hydrogenation

Catalytic converters reduce CO and NO emission.

Enzymes – selective catalysts

Enzymes are a long protein molecules that fold into balls. They often have a metal coordinated to the O and N sites.

Molecules catalyzed by enzymes are called **substrates**. They are held by various sites (together called the **active site**) of the enzyme molecules and just before and during the reaction. After having reacted, the products P_1 & P_2 are released.

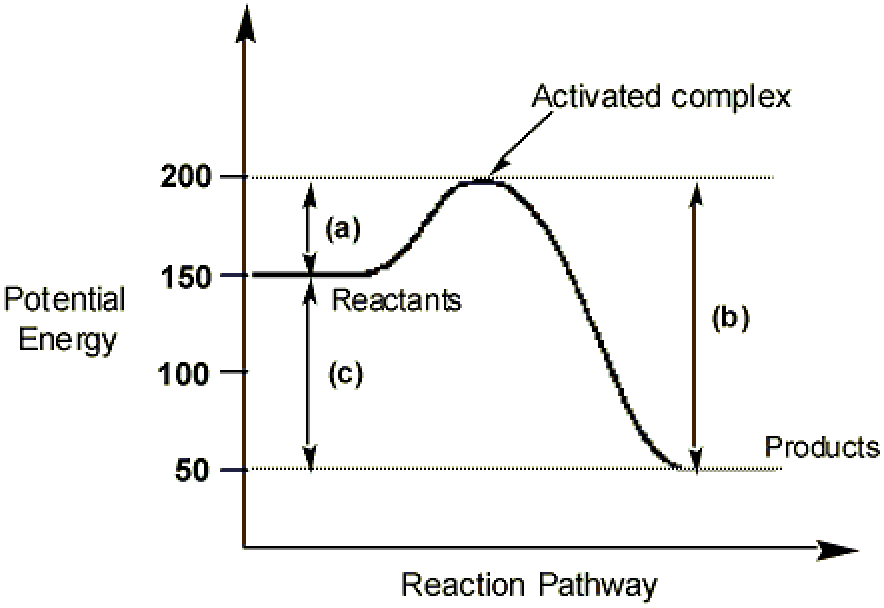


$$E_{nzyme} + S_{ubstrate} \rightarrow ES \text{ (activated complex)}$$

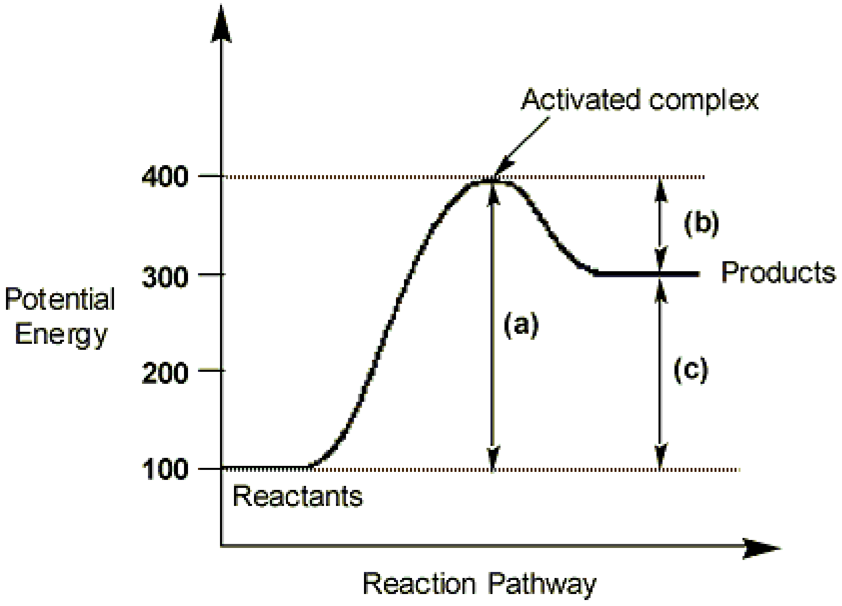
$$ES \rightarrow P_1 + P_2 + E$$

Enzymes are biological catalysts for biological systems.

Energy Diagrams



Exothermic



Endothermic

(a) Activation energy (Ea) for the forward reaction

(b) Activation energy (Ea) for the reverse reaction

(c) Delta H

50 kJ/mol	300 kJ/mol
150 kJ/mol	100 kJ/mol
-100 kJ/mol	+200 kJ/mol

Training exercises

1. Calculate $\Delta H°$ for the following reaction:

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

Given the following information:

	$\Delta H_f°$ (kJ/mol)
$Na(s)$	0
$H_2O(l)$	– 286
$NaOH(aq)$	– 470
$H_2(g)$	0

$\Delta H° = –368$ kJ

2. Predict the sign of ΔS for each of the following, and explain:

a) The evaporation of alcohol
b) The freezing of water
c) Compressing an ideal gas at constant temperature
d) Heating an ideal gas at constant pressure
e) Dissolving NaCl in water