Bangladesh University of Engineering and Technology
Department of Chemistry

CHEM113: Chemistry

For Students of CSE

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CHEM113 : Chemistry

Total Credit Hours: 3 ; L1/T2

Quantum concept in atomic structure, VSEPRT; molecular geometry, Quantum concept in bonding; VBT and MOT, Frontier MOT and electronic transition, Silicon chemistry, Properties of solutions, Colloid and Nano-chemsitry, **Phase rule and phase diagram; Energy and chemistry, Electrochemistry; electrolytic conduction, corrosion, devices for energy storage, Chemistry of biodegradable and conductive polymer; LED, LCD/touch screen,** Chemistry of proteins, nucleic acids (DNA, RNA), carbohydrates and lipids; Introduction to computational chemistry; Design of new molecules, materials and drug.
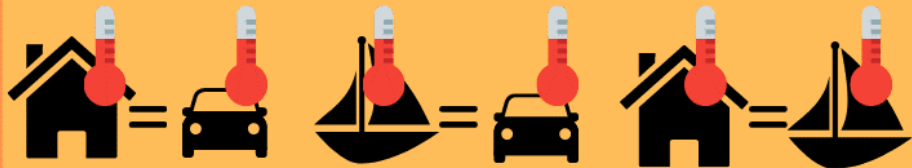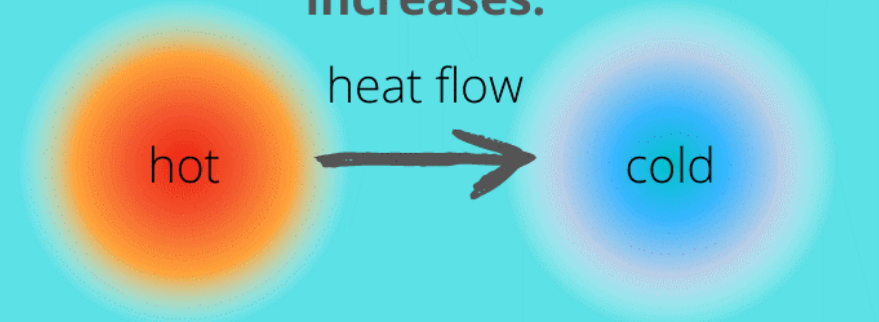
Chemical reaction and enthalpy change, ΔH
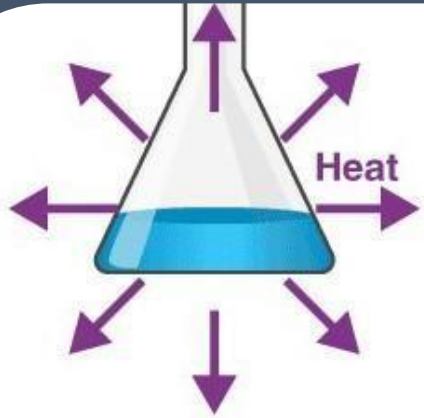
Exothermic Reactions
A reaction that releases energy from the system in the form of heat.

Endothermic Reaction
A reaction that the system absorbs energy from its surrounding in the form of heat.

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$

Methane   Oxygen   Carbon Dioxide   Water

Combustion Reaction

Thermochemical reaction and ΔH

$$C_5H_{12}(l) + 8\,O_2(g) \rightarrow 5\,CO_2(g) + 6\,H_2O(l) \qquad \Delta H^{\circ}_{rxn} = -3523\,kJ$$
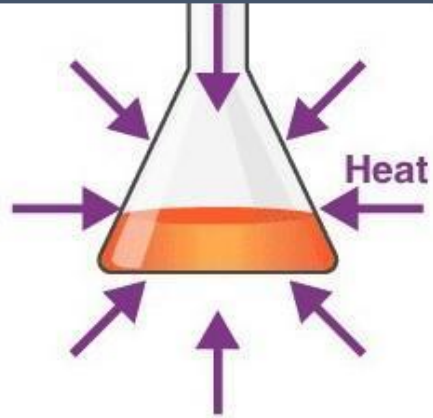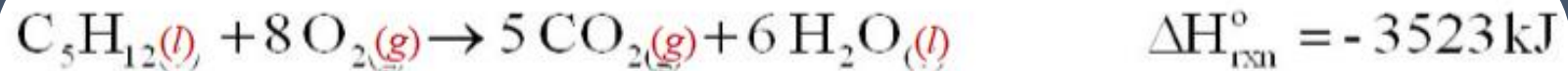
$\Delta H < 0$ designates an exothermic reaction:
heat is a product, the container feels hot

$\Delta H > 0$ designates an endothermic reaction:
heat is a reactant, the container feels cold

- The enthalpy change for a reaction depends on the state of the reactants and products

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H = -890\ kJ$
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ $\Delta H = -802\ kJ$
$2H_2O(g) \rightarrow 2H_2O(l)$ $\Delta H = -88kJ$

Thermodynamic systems and processes

Universe

Surrounding

System

System Boundary

System

surrounding

energy

system

matter

OPEN

surrounding

energy

system

CLOSED

surrounding

system

ISOLATED
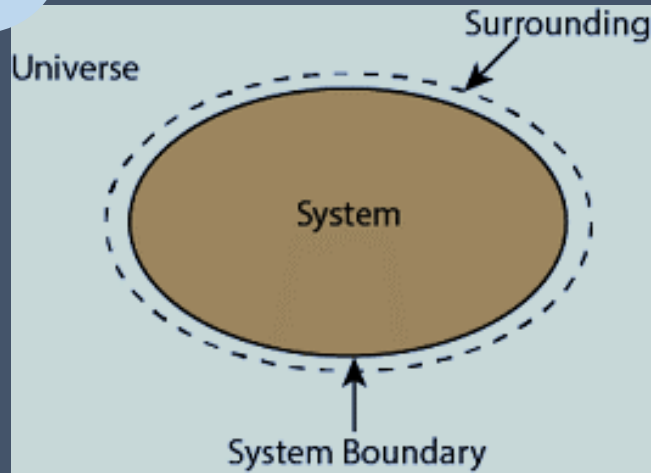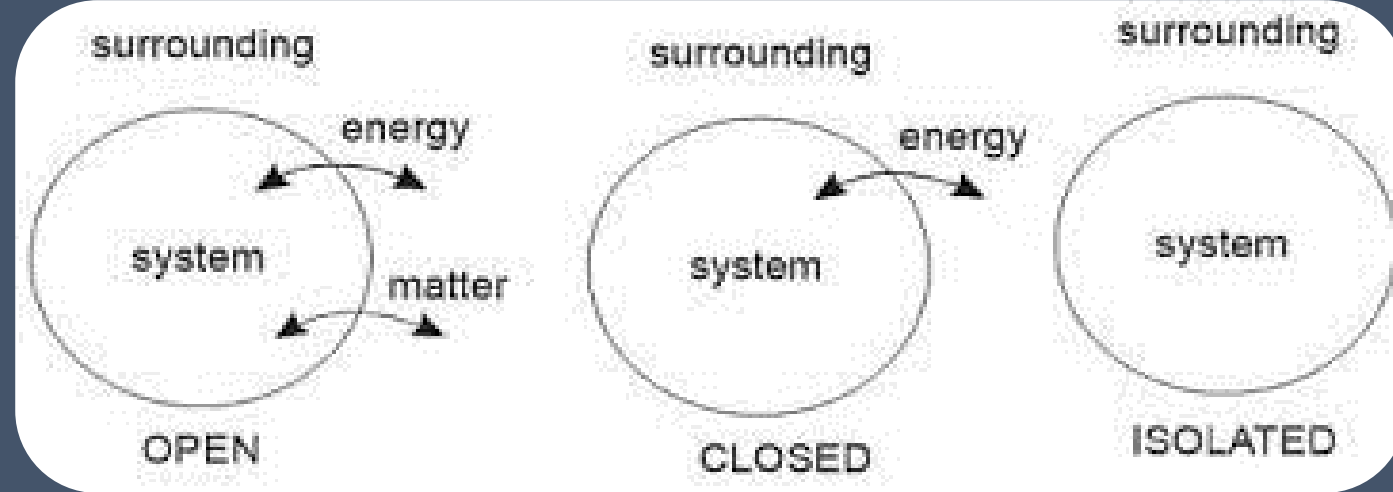
Isobaric process

Thermodynamic process in which the **pressure remains constant** is known as *isobaric process*.

Isochoric process

Thermodynamic process in which the **volume remains constant** is called *isochoric process*.

Adiabatic process
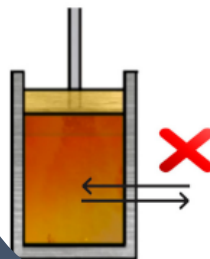
Thermodynamic process in which there is **no heat transfer** involved is called *adiabatic process*.

Isothermal process

The process in which the **temperature remains constant** is known as *Isothermal process*.

Mass

Heat

Open system
Mass transfer (yes)
Heat transfer (yes)

Mass

Heat

Closed system
Mass transfer (No)
Heat transfer (Yes)

Mass

Heat

Isolated system
Mass transfer (No)
Heat transfer (No)

Sign convention: Heat (Q) and work (W)

IUPAC
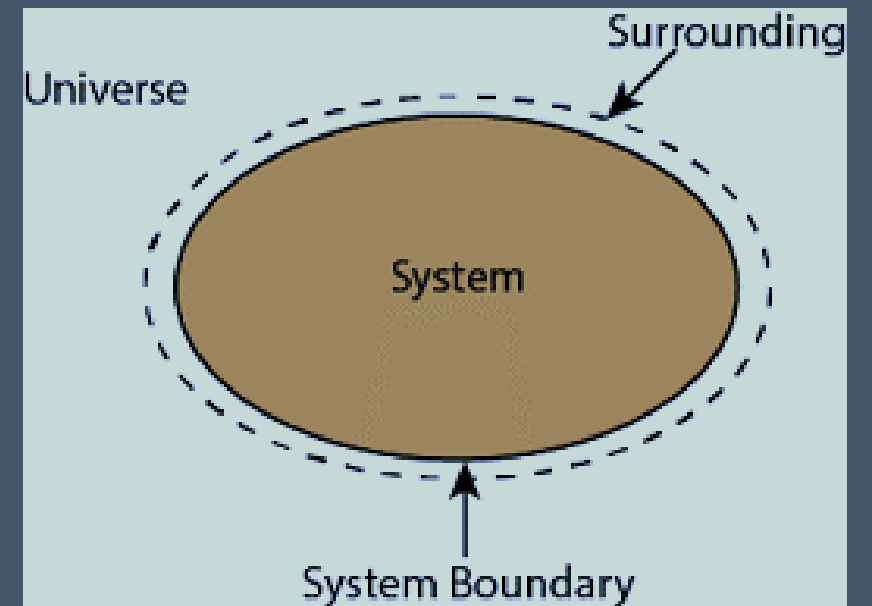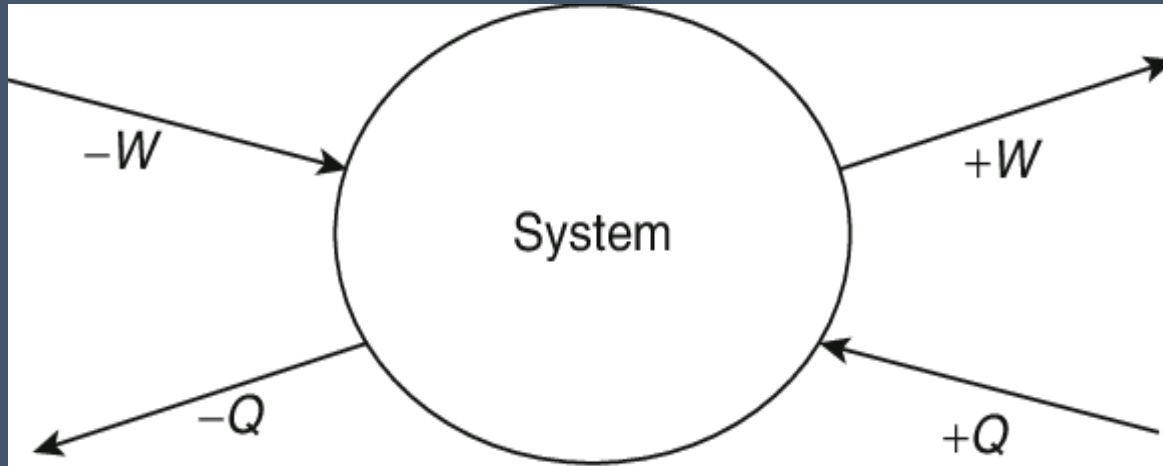
Heat Engine

A heat engine is a device that converts chemical energy to heat or thermal energy and then to mechanical energy or electrical energy. For example, automotive engines are heat engines that can consume primary energy sources.

All conventional thermal power plants are heat engines subject to the efficiency limitations imposed by the second law of thermodynamics.

A typical **gasoline** automotive engine operates at around 25% to 30% of thermal efficiency. About 70-75% is rejected as waste heat without being converted into useful work, i.e., work delivered to wheels.

Hot Source (Fuel)

Heat In
$|Q_H|$

Work Out
$|W|$

Waste Heat
$|Q_L|$

Thermal efficiency
$$\eta = \frac{|W|}{|Q_H|}$$

Atmosphere/Body of Water
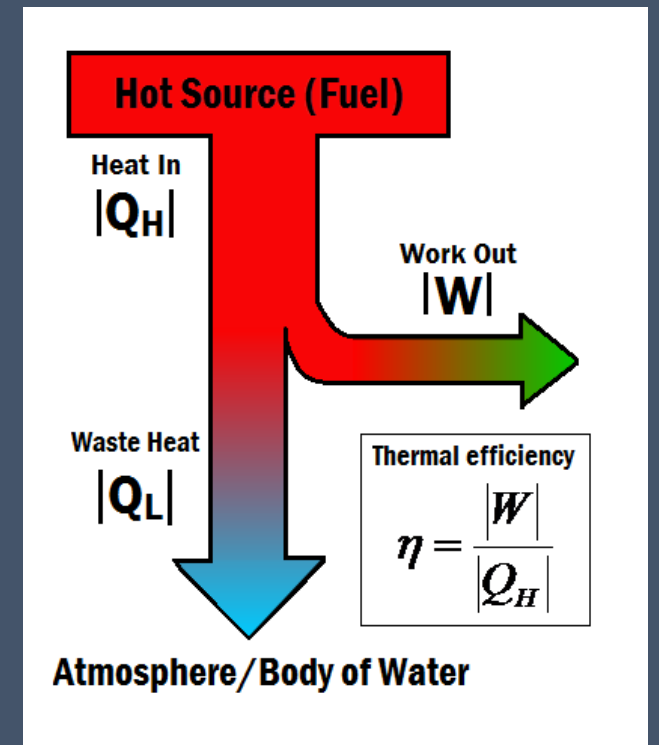
Power Plants: Heat Engines

Many heat engines operate cyclically, adding energy in the form of heat in one part of the cycle and using that energy to do useful work in another part of the cycle.

In all conventional thermal power plants, the heat is used to generate steam which drives a steam turbine connected to a generator that produces electricity. Steam generators, steam turbines, condensers, and feed-water pumps constitute a heat engine subject to the efficiency limitations imposed by the second law of thermodynamics.

In modern nuclear power plants, the overall thermodynamic efficiency is about one-third (33%), so 3000 MW of thermal power from the fission reaction is needed to generate 1000 MW of electrical power.

Steam turbine

W_T

Q_C

Condenser

Rankine cycle

Heat exchanger

Q_H

Feedwater pump W_P

$$\eta = \frac{W_T - W_P}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$
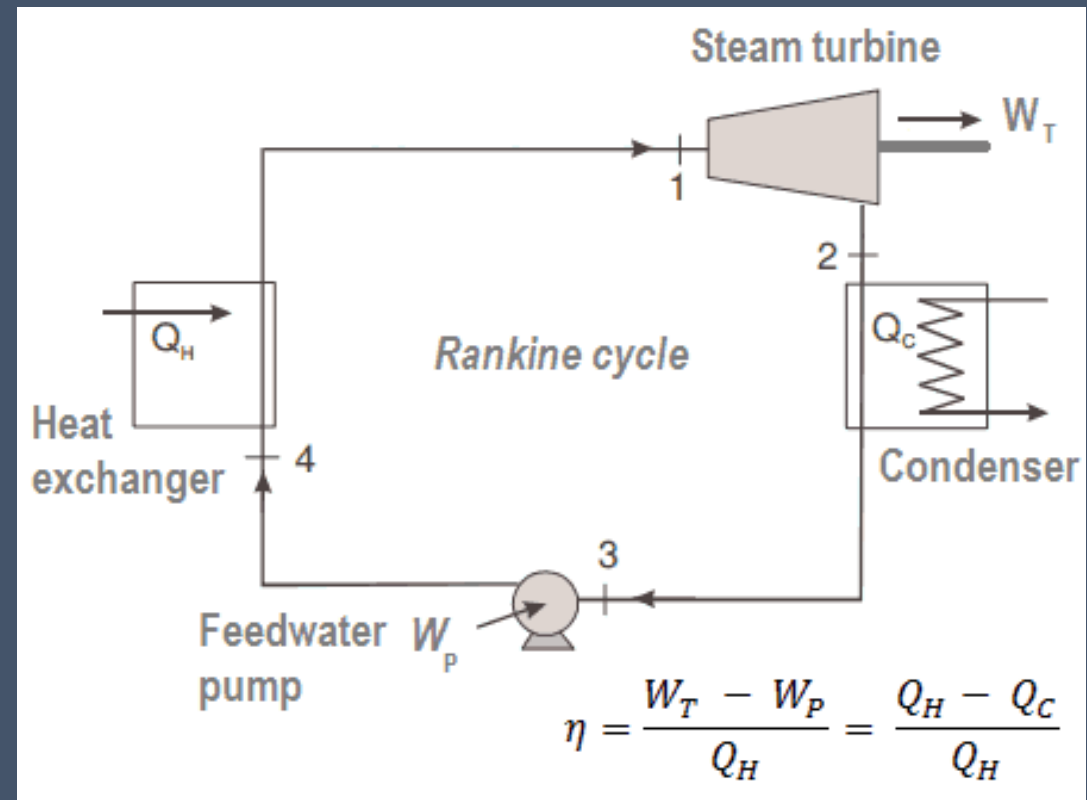
Heat Engines: Efficiency

Thermal efficiency

An ideal heat engine is an imaginary engine in which energy extracted as heat from the high-temperature reservoir is converted completely to work. But according to the Kelvin-Planck statement, such an engine would violate the second law of thermodynamics because there must be losses in the conversion process. The net heat added to the system must be higher than the net work done by the system.

Kelvin-Planck statement: "It is impossible to construct a device which operates on a cycle and produces no other effect than the production of work and the transfer of heat from a single body".

Heat Engines: Efficiency

In this case, steam generators, steam turbines, condensers, and feed water pumps constitute a heat engine subject to the efficiency limitations imposed by the second law of thermodynamics. In an ideal case (no friction, reversible processes, perfect design), this heat engine would have a Carnot efficiency of

$= 1 - (T_{cold} / T_{hot)} = 1 - (315/549) = 42.6\%$

where the temperature of the hot reservoir is 275.6 °C (548.7 K), the temperature of the cold reservoir is 41.5 °C (314.7 K). But the nuclear power plant is the real heat engine, in which thermodynamic processes are somehow irreversible. They are not done infinitely slowly. In real devices (turbines, pumps, and compressors), mechanical friction and heat losses cause further efficiency losses.

$$\eta_{th} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

Heat Engines: Efficiency

Transportation

In the middle of the twentieth century, a typical steam locomotive had a thermal efficiency of about 6%. That means for every 100 MJ of coal burned, 6 MJ of mechanical power were produced.

A typical gasoline automotive engine operates at around 25% to 30% of thermal efficiency. About 70-75% is rejected as waste heat without being converted into useful work, i.e., work delivered to wheels.

A typical diesel automotive engine operates at around 30% to 35%. In general, engines using the Diesel cycle are usually more efficient.

In 2014, new regulations were introduced for Formula 1 cars. These motorsport regulations have pushed teams to develop highly efficient power units. According to Mercedes, their power unit is now achieving more than 45% and close to 50% thermal efficiency, i.e., 45 – 50% of the potential energy in the fuel is delivered to wheels.
The diesel engine has the highest thermal efficiency of any practical combustion engine. Low-speed diesel engines (as used in ships) can have a thermal efficiency that exceeds 50%. The largest diesel engine in the world peaks at 51.7%.

Heat Engines: Efficiency

Power Engineering

Ocean thermal energy conversion (OTEC). OTEC is a sophisticated heat engine that uses the temperature difference between cooler deep and warmer surface seawaters to run a low-pressure turbine. Since the temperature difference is low, about 20°C, **its thermal efficiency is also very low, about 3%.**

In modern nuclear power plants, the overall thermal efficiency is about one-third (33%), so 3000 MWth of thermal power from the fission reaction is needed to generate 1000 MWe of electrical power. In comparison to other energy sources, the thermal efficiency of 33% is not much. But it must be noted that nuclear power plants are much more complex than fossil fuel power plants, and it is much easier to burn fossil fuel than to generate energy from nuclear fuel.

Sub-critical fossil fuel power plants that are operated under critical pressure (i.e., lower than 22.1 MPa) can achieve 36–40% efficiency.

Supercritical fossil fuel power plants operated at supercritical pressure (i.e., greater than 22.1 MPa) have efficiencies of around 43%. Most efficient and complex coal-fired power plants operate at "ultra critical" pressures (i.e., around 30 MPa) and use multiple stage reheat to reach about 48% efficiency.

Modern Combined Cycle Gas Turbine (CCGT) plants, in which the thermodynamic cycle consists of two power plant cycles (e.g.,, the Brayton cycle and the Rankine cycle), can achieve a thermal efficiency of around 55%, in contrast to a single cycle steam power plant which is limited to efficiencies of around 35-45%.

Heat Engines: Causes of Inefficiency

Efficiency can range between 0 and 1.

Irreversibility of Processes: There is an overall theoretical upper limit to the efficiency of conversion of heat to work in any heat engine. This upper limit is called the Carnot efficiency. According to the Carnot principle, no engine can be more efficient than a reversible engine (Carnot heat engine) operating between the same high temperature and low-temperature reservoirs. For example, when the hot reservoir has T_{hot} of 400°C (673K) and T_{cold} of about 20°C (293K), the maximum (ideal) efficiency will be 56%. But all real thermodynamic processes are somehow irreversible. They are not done infinitely slowly. Therefore, heat engines must have lower efficiencies than limits on their efficiency due to the inherent irreversibility of the heat engine cycle they use.

Presence of Friction and Heat Losses: In real heat engines, a part of the overall cycle inefficiency is due to the losses by the individual components. In real devices (such as turbines, pumps, and compressors), mechanical friction, heat losses, and losses in the combustion process cause further efficiency losses.

Design Inefficiency: The important source of inefficiencies is the compromises made by engineers when designing a heat engine (e.g.,, power plant). They must consider cost and other factors in the design and operation of the cycle. As an example, consider the design of the condenser in the thermal power plants. Ideally, the steam exhausted into the condenser would have no sub-cooling. But real condensers are designed to sub-cool the liquid by a few degrees Celsius to avoid the suction cavitation in the condensate pumps. But, this sub-cooling increases the inefficiency of the cycle because more energy is needed to reheat the water.

Gibbs free energy

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

Exergonic and endergonic reactions

Exergonic and endergonic reaction

Exergonic and endergonic refer to changes in the Gibbs free energy, ΔG

Exothermic and endothermic refer to changes in enthalpy, ΔH

We can express the spontaneity of a reaction <u>at constant temperature and pressure</u> in terms of the reaction Gibbs energy:

If $\Delta_r G < 0$, the forward reaction is spontaneous.

If $\Delta_r G > 0$, the reverse reaction is spontaneous.

If $\Delta_r G = 0$, the reaction is at equilibrium.

A reaction for which $\Delta_r G < 0$ is called exergonic (from the Greek words for work-producing). The name signifies that, because the process is spontaneous, it can be used to drive another process, such as another reaction, or used to do non-expansion work.

Exergonic and endergonic reactions

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

We have four possibilities:

Case I. $\Delta H < 0$ and $\Delta S > 0$ always gives $\Delta G < 0$.
The process is both **exothermic** **and** **exergonic**.
It is always spontaneous.

Case II. $\Delta H > 0$ and $\Delta S < 0$ always gives $\Delta G > 0$.
The process is both **endothermic** **and** **endergonic**.
It is *never* spontaneous.

Case III. $\Delta H > 0$ and $\Delta S > 0$.

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

This gives $\Delta G > 0$ *at low temperatures*. The process is both **endothermic** and **endergonic**.

At high temperatures, $\Delta G < 0$. The process is still endothermic but it has become exergonic. The process is spontaneous only at high temperatures.

An example is the endothermic decomposition of calcium carbonate.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

ΔS is positive because the reaction produces a gas from a solid. $CaCO_3$ is stable at room temperature, but decomposes at high temperatures.

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

Case IV. $\Delta H < 0$ **and** $\Delta S < 0$.

This gives $\Delta G < 0$ *at low temperatures*. The process is both **exothermic** and **exergonic**.

At high temperatures, $\Delta G > 0$. The process is still ***exothermic*** but it has become ***endergonic***. **It is no longer spontaneous.**

An example is the exothermic synthesis of ammonia.

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$$

Increasing the temperature increases the yield of ammonia. But it drives the position of equilibrium to the left.

Nobel prize in 1918

# Spontaneity of a reaction

Conditions_ At a glance

ΔH	ΔS	ΔG	Reaction Spontaneity
Negative	Positive	Negative	Always spontaneous
Negative	Negative	Negative or positive	Spontaneous at low temperatures
Positive	Positive	Negative or positive	Spontaneous at high temperatures
Positive	Negative	Positive	Never spontaneous

Coupled reactions: Biological cells

Coupled reactions are a thermodynamic concept where a thermodynamically unfavorable reaction (one with $\Delta G > 0$) is made to proceed *by linking it* to a thermodynamically favorable reaction ($\Delta G < 0$). The favorable reaction provides energy that drives the unfavorable one, making the overall process spontaneous.
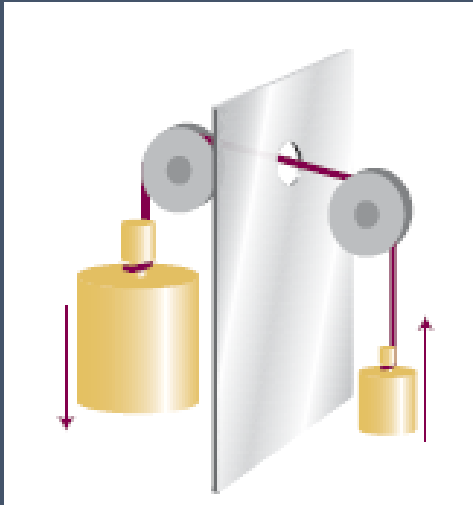
A simple mechanical analogy is a pair of weights joined by a string (Fig): the lighter of the pair of weights will be pulled up as the heavier weight falls down. Although the lighter weight has a natural tendency to move downward, its coupling to the heavier weight results in it being raised.

In biological cells, the oxidation of carbohydrates act as the heavy weight that drives other reactions forward and results in the formation of proteins from amino acids, muscle contraction, and brain activity.
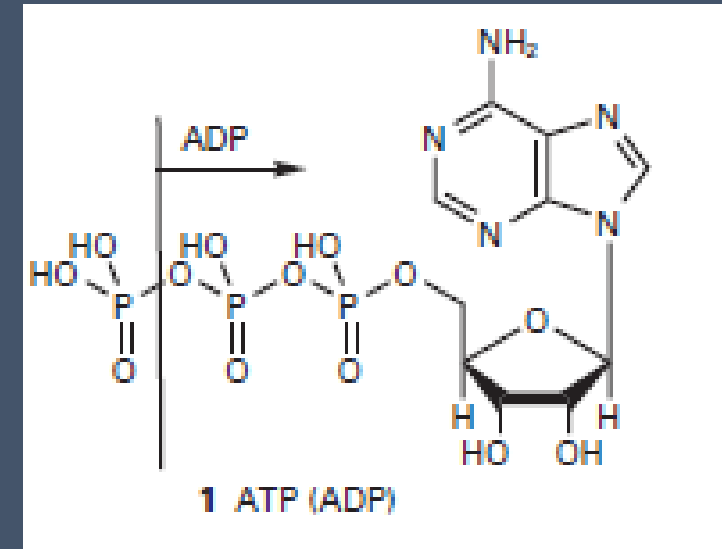
Thermodynamics of ATP

$$\Delta_r G^\otimes = \Delta_r H^\otimes - T\Delta_r S^\otimes$$

$$\text{ATP(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{ADP(aq)} + \text{P}_i^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$

1 ATP (ADP)

ATP : Adenosine triphosphate

where P_i^- denotes an inorganic phosphate group, such as $H_2PO_4^-$. The biological standard values for ATP hydrolysis at 37°C (310 K, blood temperature) are $\Delta_r G^\oplus = -31$ kJ mol^{-1}, $\Delta_r H^\oplus = -20$ kJ mol^{-1}, and $\Delta_r S^\oplus = +34$ J K^{-1} mol^{-1}. The hydrolysis is, therefore, exergonic ($\Delta_r G^\oplus < 0$) under these conditions and 31 kJ mol^{-1} is available for driving other reactions.
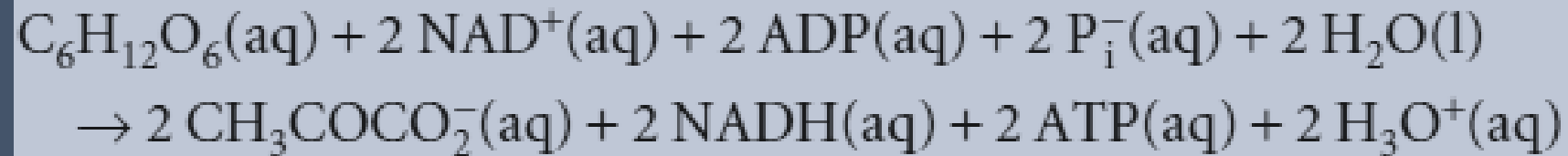
Moreover, because the reaction entropy is large, the reaction Gibbs energy is sensitive to temperature. In view of its exergonicity the ADP-phosphate bond has been called a '*high-energy phosphate bond*'. The name is intended to signify a high tendency to undergo reaction, and should not be **confused** with 'strong' bond. In fact, even in the biological sense it is not of very 'high energy'. The action of ATP depends on it being intermediate in activity. Thus, ATP acts as a phosphate donor to a number of acceptors (for example, glucose), but is recharged by more powerful phosphate donors in a number of biochemical processes.
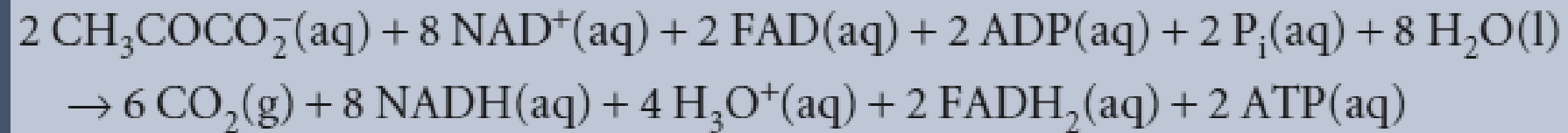
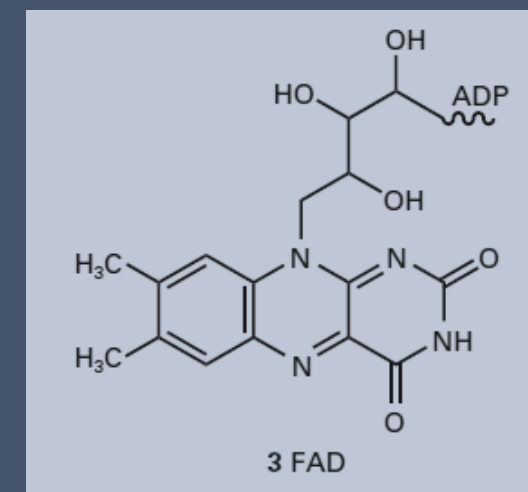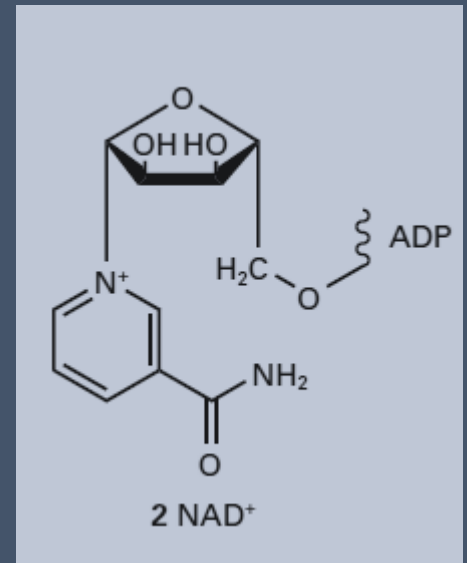# Biological energy conversion: The oxidation of glucose

Anaerobic : Glycolysis

$$C_6H_{12}O_6(aq) + 2\,NAD^+(aq) + 2\,ADP(aq) + 2\,P_i^-(aq) + 2\,H_2O(l)$$
$$\rightarrow 2\,CH_3COCO_2^-(aq) + 2\,NADH(aq) + 2\,ATP(aq) + 2\,H_3O^+(aq)$$

Aerobic

$$2\,CH_3COCO_2^-(aq) + 8\,NAD^+(aq) + 2\,FAD(aq) + 2\,ADP(aq) + 2\,P_i(aq) + 8\,H_2O(l)$$
$$\rightarrow 6\,CO_2(g) + 8\,NADH(aq) + 4\,H_3O^+(aq) + 2\,FADH_2(aq) + 2\,ATP(aq)$$

NADH : Nicotinamide adenine dinucleotide

FAD : Flavin adenine dinucleotide

2 NAD+

3 FAD
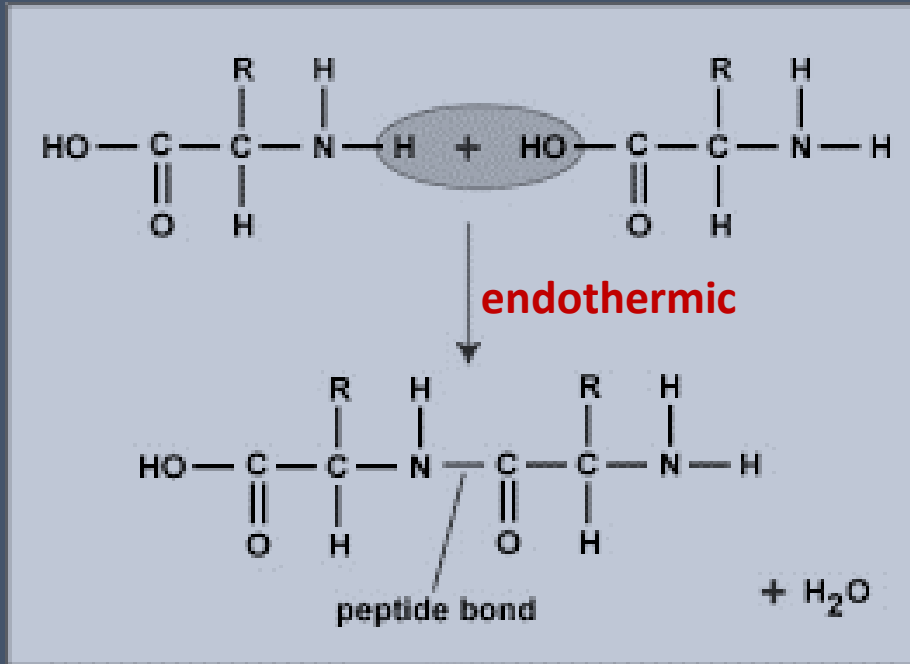
Biological energy conversion: Synthesis of proteins

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

$\Delta H > 0$ and $\Delta S < 0$ always gives $\Delta G > 0$.

The process is both **endothermic** and **endergonic.**

endothermic

peptide bond

$+ H_2O$

$\Delta_r G^\oplus = +17$ kJ mol^{-1}

Since, $\Delta_r H^\oplus = +ve$, and $\Delta_r S^\oplus = -ve$???

1 peptide link $\equiv$ 3 ATP

Small protein with 150 peptide links (myoglobin) $\equiv$ 450 ATP $\equiv$ about 12 glucose