

Thermochemistry, thermodynamics

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Thermochemistry

In thermochemistry we study the energy changes that accompany physical and chemical processes.

- ▶ Energy is the capacity to do work or to transfer heat.
- ▶ Kinetic energy is the energy of motion:

$$E_{kinetic} = \frac{1}{2}mv^2$$

- ▶ Potential energy is the energy that a system possesses by virtue of its position or composition.
- ▶ Heat is the form of energy that always flows spontaneously from a hotter body to a colder body – it never flows in the reverse direction.

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Thermochemistry, thermodynamics

In thermodynamics we study the energy changes that accompany physical and chemical processes.

- ▶ Chemical reactions and physical changes occur with either the simultaneous evolution of heat (exothermic process) or the absorption of heat (endothermic process).
- ▶ The specific heat of a substance is the amount of heat required to raise the temperature of one gram of the substance one degree Celsius with no changes in phase. The units of specific heat is $\frac{\text{J}}{\text{g}\cdot^{\circ}\text{C}}$.

$$Q_p = c_p m \Delta T \text{ at constant pressure}$$

$$Q_V = c_V m \Delta T \text{ at constant volume}$$

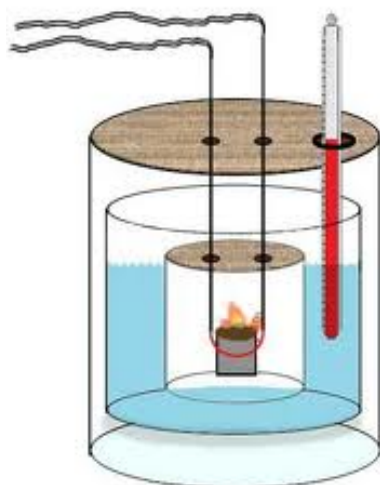
- ▶ The heat capacity of a body is the amount of heat required to raise its temperature 1 °C.

$$Q_p = C_p \Delta T \text{ at constant pressure}$$

$$Q_V = C_V \Delta T \text{ at constant volume}$$

Calorimetry

A calorimeter is a device used for calorimetry, the science of measuring the heat of chemical reactions or physical changes as well as heat capacity. A simple calorimeter just consists of a thermometer attached to a metal container full of water suspended above a combustion chamber.



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$$Q = C_{\text{water}}\Delta T$$

Some Thermodynamic Terms

- ▶ The substances that we are studying are called the system.
- ▶ Everything in the system's environment constitutes its surroundings.
- ▶ The thermodynamic state of a system is defined by a set of conditions that completely specifies all the properties of the system. This set commonly includes the temperature, pressure, composition, and physical state (gas, liquid or solid) of each part of the system. The properties of a system – such as P , V , T – are called state functions.
- ▶ The internal energy of a system represents all the energy contained within the system. It includes the kinetic energies of the molecules, energies of attraction and repulsion among subatomic particles, atoms, ions and molecules; and other forms of energy.

First Law of Thermodynamics

The first law of thermodynamics is the law of conservation of energy: energy can be converted from one form into another but it cannot be created or destroyed. The total energy of the universe is a constant.

The change of the internal energy of a system:

$$\Delta E = q + w$$

- ▶ q is positive: Heat is absorbed by the system from the surroundings.
- ▶ q is negative: Heat is released by the system to the surroundings.
- ▶ w is positive: Work is done on the system by the surroundings.
- ▶ w is negative: Work is done by the system on the surroundings.

First Law of Thermodynamics

The work done in expansion from V_1 to V_2 at constant pressure:

$$w = -p(V_2 - V_1) = -p\Delta V$$

Compression: work is done by the surroundings on the system. V_2 is less than V_1 , so $\Delta V < 0$ and $w > 0$.

Expansion: work is done by the system on the surroundings. V_2 is greater than V_1 , so $\Delta V > 0$ and $w < 0$.

Changes in Internal Energy

In constant-volume processes $w = 0$ Thus, the equation

$$\Delta E = q + w$$

becomes

$$\Delta E = q_w$$

The change in the internal energy is just the amount of heat absorbed or released at constant volume.

Changes in Internal Energy

Most chemical reactions and physical changes occur at constant (usually atmospheric) pressure.

In constant-pressure processes the equation

$$\Delta E = q + w$$

becomes

$$\Delta E = q_p - p\Delta V$$

The quantity of heat transferred into or out of a system as it undergoes a chemical or physical change at constant pressure, q_p , is defined as the enthalpy change, ΔH , of the process.

$$q_p = \Delta H = \Delta E + p\Delta V \text{ (constant } T, p)$$

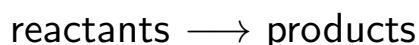
Standard States

The thermodynamic standard state of a substance is its most stable pure form under standard pressure (1 bar) and some specific temperature (298 K unless otherwise specified).

- ▶ For a pure substance in the liquid or solid phase, the standard state is the pure liquid or solid (C(graphite), H₂O(l), CaCO₃(s)).
- ▶ For a gas, the standard state is the gas at a pressure of one atmosphere; in the mixture of gases, its partial pressure must be one atmosphere.
- ▶ For, a substance in solution, the standard state refers to one-molar concentration.

Standard States

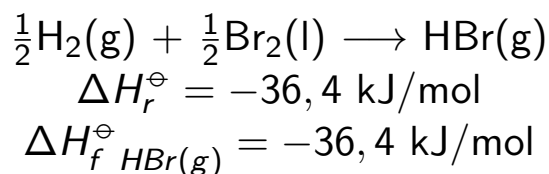
The standard enthalpy change, ΔH_r^\ominus , for a reaction



refers to the ΔH when specified number of moles of reactants, all at standard states, are converted completely to the specified number of moles of products, all at standard states.

Standard States

The standard molar enthalpy of formation (heat of formation), ΔH_f^\ominus , of a substance is the enthalpy change from the reaction in which one mole of the substance in a specified state is formed from its elements in their standard states. By convention, the ΔH_f^\ominus value for any element in its standard state is zero.



Standard States

reactants \longrightarrow products

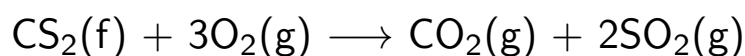
The standard enthalpy change of a reaction is equal to the sum of the standard molar enthalpies of formation of the products, minus the corresponding sum of the standard molar enthalpies of formation of the reactants.

$$\Delta H_r^\ominus = \sum \Delta H_f^\ominus_{\text{products}} - \sum \Delta H_f^\ominus_{\text{reactants}}$$

Standard enthalpy change for a reaction

Example:

Calculate the standard enthalpy change of ignition of CS₂.



$$\Delta H_f^\ominus(\text{CO}_2(\text{g})) = -393.5 \text{ kJ/mol}, \Delta H_f^\ominus(\text{SO}_2(\text{g})) = -296.8 \text{ kJ/mol}$$

$$\Delta H_f^\ominus(\text{CS}_2(\text{f})) = +87,9 \text{ kJ/mol}$$

$$\Delta H_r^\ominus = \sum \Delta H_f^\ominus_{\text{products}} - \sum \Delta H_f^\ominus_{\text{reactants}}$$

$$\Delta H_r^\ominus = \Delta H_f^\ominus(\text{CO}_2(\text{g})) + 2\Delta H_f^\ominus(\text{SO}_2(\text{g})) - \Delta H_f^\ominus(\text{CS}_2(\text{f})) - 3\Delta H_f^\ominus(\text{O}_2(\text{f}))$$

$$\Delta H_r^\ominus = (-393.5 + 2 \cdot 296.8) - (87.9 + 0) = -1057 \text{ kJ/mol}$$

Hess's Law

G. H. Hess (1802-1850)

The enthalpy change for a reaction is the same whether it occurs by one step or by series of steps. Enthalpy is a state function. Its change is therefore independent of the pathway by which a reaction occurs.

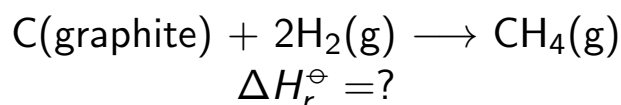
$$\Delta H_r^\ominus = \Delta H_a^\ominus + \Delta H_b^\ominus + \Delta H_c^\ominus + \dots$$

Here a, b, c... refer to balanced equations that can be summed to give the equation for the desired reaction.

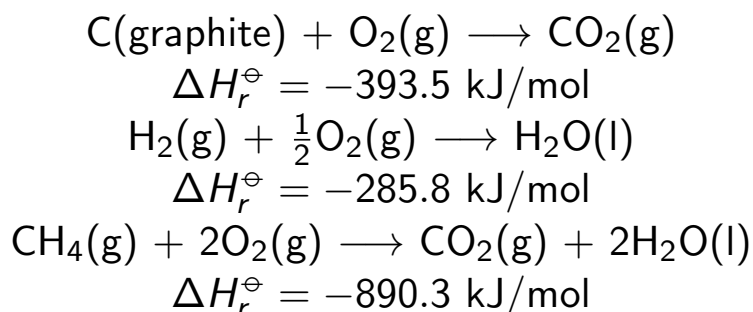
Hess's Law

Example

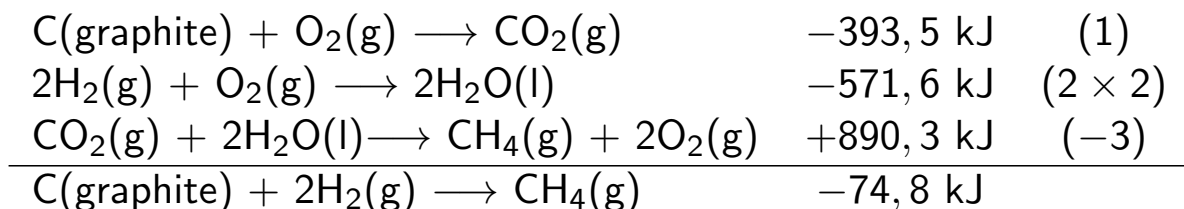
Calculate the standard enthalpy change of the this reaction:



if we know the standard enthalpy change of these reactions:



Hess's Law



The Second Law of Thermodynamics

Two factors affect the spontaneity of any physical or chemical change:

- ▶ Spontaneity is favored when heat is released during the change (exothermic)
- ▶ Spontaneity is favored when the change causes an increase in disorder

The thermodynamic state function entropy, S , is a measure of the disorder of the system. Entropy of an isolated system increases during a spontaneous process:

$$\Delta S_{tot} > 0$$

Entropy

During a spontaneous process:

$$\Delta S(\text{system}) + \Delta S(\text{surroundings}) > 0$$

In a reversible process (a process proceeding only through equilibrium states):

$$\Delta S_{rev} = \frac{q_{rev}}{T}$$

In an irreversible process:

$$\Delta S > \frac{q}{T}$$

In a constant volume irreversible process:

$$\Delta U = q_v \leq T\Delta S$$

Third Law of Thermodynamics

The entropy of a pure, perfect crystalline substance is zero at absolute zero (0 K).

$$\Delta S \rightarrow 0, \text{ if } T \rightarrow 0$$

The entropy of a substance at any condition is its absolute entropy, also called standard molar entropy. The reference state for absolute entropy is specified by the third law of thermodynamics.

It is different from the reference state for ΔH_f^0

The standard entropy change, ΔS_r^0 , of a reaction can be determined from the absolute entropies of reactants and products:

$$\Delta S_r^0 = \sum nS_{\text{products}}^0 - \sum nS_{\text{reactants}}^0$$

Entropy

Processes that results in predictable entropy changes for the system:

- ▶ Phase changes (e.g.. melting $\Delta S(\text{system}) > 0$, freezing $\Delta S(\text{system}) < 0$)
- ▶ Temperature and volume changes
- ▶ Mixing of substances
- ▶ Increase in the number of particles
- ▶ Changes in the number of moles of gaseous substances

Gibbs function

In a constant pressure process:

$$\Delta H = q_p$$

$$\Delta H \leq T\Delta S$$

Gibbs free energy:

$$G = H - TS$$

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

Gibbs function

In a constant pressure process: The amount by which the Gibbs free energy decreases is the maximum useful energy obtainable in the form of work from a given process at constant temperature and pressure.

$$\Delta H = q + w + p\Delta V \text{ (constant } p)$$

In a reversible process (constant T)

$$q = T\Delta S$$

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

$$\Delta G = T\Delta S + w + p\Delta V - T\Delta S$$

Gibbs function

the work:

$$w = w_{\text{useful}} - p\Delta V$$

$$\Delta G = w_{\text{useful}} - p\Delta V + p\Delta V$$

$$\Delta G = w_{\text{useful}} \text{ (constant } p, T)$$

Gibbs function

The Gibbs free energy is the indicator of spontaneity of a reaction or physical change at constant T and p . If ΔG is negative the process is spontaneous (product favored reaction).

$$\Delta G \leq 0$$

1. $\Delta G < 0$ reaction is spontaneous (product favored)
2. $\Delta G > 0$ reaction is nonspontaneous (reactant favored)
3. $\Delta G = 0$ system is at equilibrium

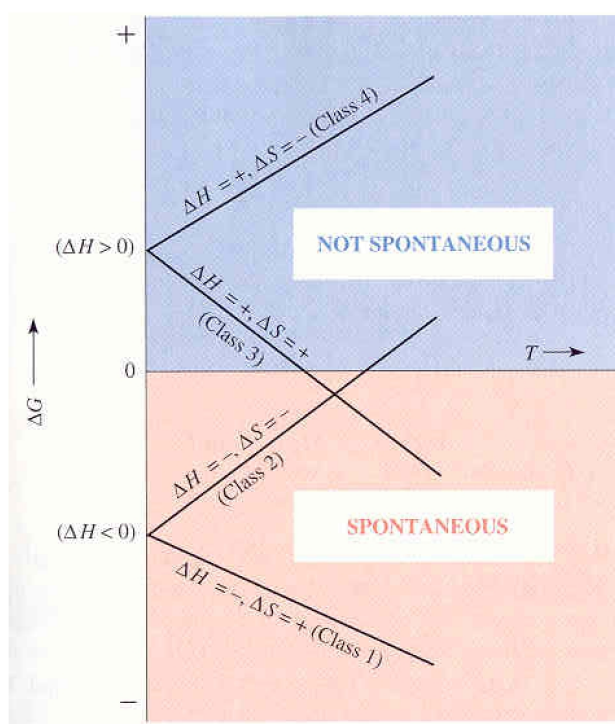
Spontaneity of Reactions

$$\Delta G = \Delta H - T\Delta S, \text{ (constant } p, T)$$

ΔH	ΔS	
-	+	Reactions are product-favored at all temperatures
-	-	Reactions become product-favored below a definite temperature
+	+	Reactions become product-favored above a definite temperature
+	-	Reactions are reactant-favored at all temperatures

Spontaneity of Reactions

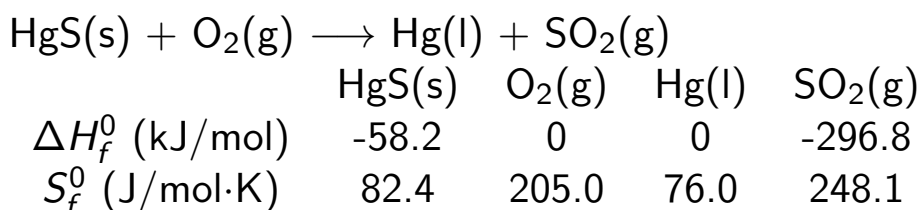
$$\Delta G = \Delta H - T\Delta S, \text{ (constant } p, T)$$



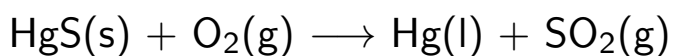
Spontaneity of Reactions

Example:

Estimate the temperature range in which the standard reaction is product-favored.



Spontaneity of Reactions



$$\Delta H_r^\circ = 0 - 296.8 - (-58.2 + 0) = -238.6 \text{ kJ/mol}$$

$$\Delta S_r^\circ = 76.02 + 248.1 - (82.4 + 205.0) = +36.7 \text{ J/molK}$$

The reaction is product-favored at all temperatures. The reverse reaction is, therefore, nonspontaneous at all temperature.

Relationship between ΔG_r^0 and K

$$\Delta G_r^0 = -RT \ln K$$

$\Delta G_r^0 < 0$	$K > 1$	products favored over reactants at equilibrium
$\Delta G_r^0 = 0$	$K = 1$	(very rare)
$\Delta G_r^0 > 0$	$K < 1$	reactants favored over products at equilibrium