Thermodynamics (Part 1)

Physical chemistry

Physical chemistry studies chemical processes along with their physical effects. It establishes connection between chemical and physical properties of the matter. Physical chemistry joins chemistry, physics and mathematics that allow creating mathematical models of the biological systems and making quantitative accounts to carry out of the process.

Physical chemistry

Physical chemistry studies all the systems, where chemical reactions can take place. It tries to solve the problem of the direction and limit of the process, to determine the rate of the process and factors, influencing the rate, optimal conditions for the process realization. By physical chemistry laws one can work out scientific foundation of the chemical and pharmaceutical technology, to find ways for manage the process. It helps to find new ways for new drug synthesis.

Thermodynamics

Thermodynamics studies heat, work, energy and their changes during a process, occurred in the system, hi a broader sense, thermodynamics studies the relationships between macroscopic properties of a system.

Thermodynamics deals with:

- the conversion of energy from one form to another:
- the energy effect in physical and chemical processes and their dependence on the conditions under which a process takes place;
- the possibility, direction and limits of spontaneous process (process, in which work and energy are not supplied from outside of system);
- determination of the conditions of equilibrium;
- amount of maximum useful work that could be obtained from the
- given process.

Chemical Thermodynamics

Chemical Thermodynamics deals with the transformation between chemical energy and other forms of energy. It studies direction and possibility of the chemical process and calculates heat effect of the reaction.

Thermodynamically methods

Thermodynamically methods and calculations have a great advantage, because they allow to know heat amounts absorbed or escaped during the process (i.e., to define amount of wasted energy or energy consumption), possibility and direction of the process without knowing its microscopic mechanisms and without making experiments.

Thermodynamically methods

Thermodynamic method has two demerits.

- First deals only with macroscopic systems consisting of large quantity of particles.
- Second demerit is that time as a parameter is absent in thermodynamic equations. That means that the thermodynamics can give no information concerning the rate of a process.

Definitions

The system is a body or a group of interacting bodies that we consider apart from its surrounding. It may be a reaction vessel, an engine, a biological cell, and so on.

- The **open system** is a system which exchanges energy and substance with environment (ex.: a man).
- The **closed system** is a system which exchanges energy only (ex.: the heated stone).
- The **isolated system** is a system, which exchanges nothing (the thermoflask).
- An adiabatic system cannot exchange the heat with its surroundings.

Definitions

- The **homogeneous system** consists of one phase. The **heterogeneous system** consists of two or more phases.
- The **condition of the system** is any physical or chemical property of the system, such as thermal capacity, eternal energy, entropy, etc.
- The **parameter of the system** is a thermal property which is easily expressed by the practical way (p, n, T).

Definitions

- The parameters describing the conditions of the system are functions of the condition. Their main property is independence on ways of their changes.
- The **extensive parameters** depend on mass of the system (thermal capacity, internal energy, volume, entropy). The **intensive parameters** do not depend on mass of the system (temperature, pressure).
- The transition of the system from one state to another is called the **thermodynamic process.**

Definitions

- When a state of a thermodynamic system is changed, we say a thermodynamic process occurs in a system. There are a few types of thermodynamic processes.
- **In a cyclic process** the final state is the same as the initial state. The change in any state function for a cyclic process is obviously zero
- **Spontaneous process** takes place without work being done on the system. This process occurs only at the expense of the own energy reserve of the system (without energy entry from the surroundings). It happens naturally: a gas expands to fill the available volume, a hot body cools to the temperature of its surroundings, a body falls from a higher level to a lower one, etc.
- **Nonspontaneous process** must be brought about by doing work to the system: compression a gas to a smaller volume, cools an object with a refrigerator. In closed system every spontaneous process finishes in equilibrium state.
- A state of a system that remains constant in time without the intervention of any external process is called an **equilibrium state.**

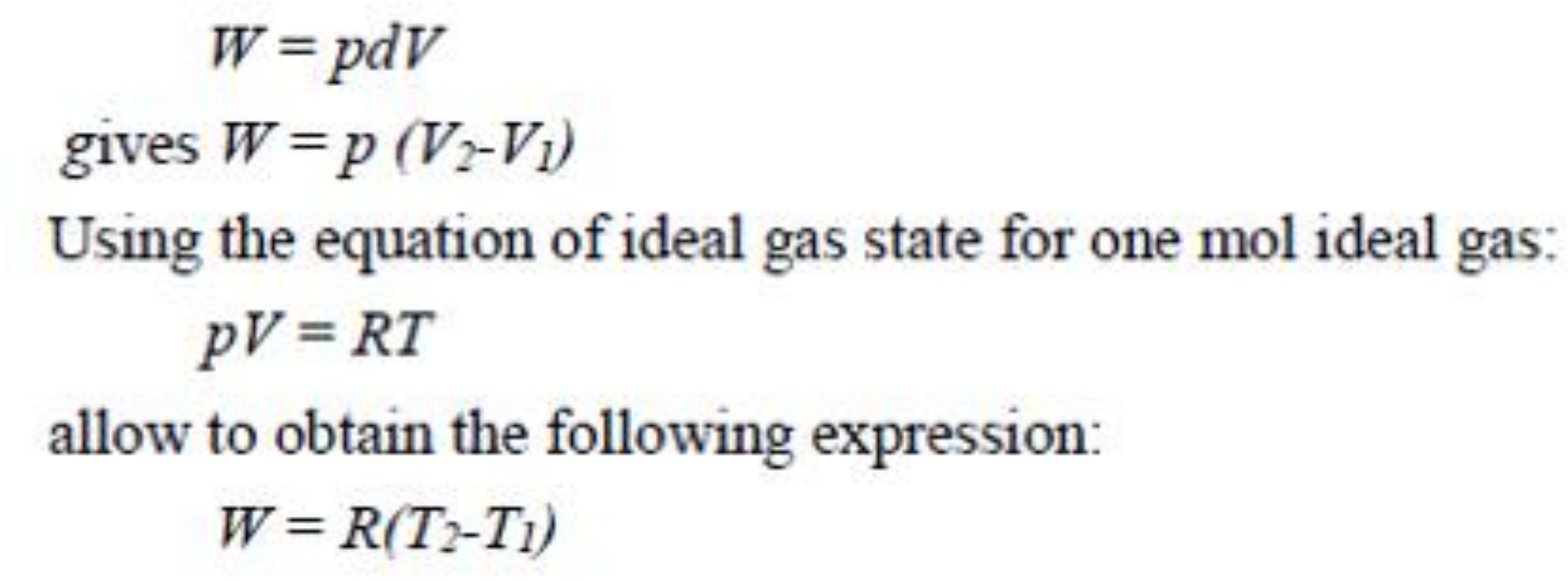
Definitions

The internal energy (U) is total kinetic and potential energy of the particles (molecules, atoms) composing the system. It does not include the kinetics of motion of the whole system or its potential energy. The internal energy depends both on the amount of the substance and on the conditions under which the process takes place. It’s a state function and an extensive property of a system.

Definitions

- Heat and work are forms of energy transfer.
- **Heat**, **q**, is an energy transfer between the system and surroundings due to a tem-perature difference and be realized by chaotic motion of molecules.
- **Work**, **W**, is an energy transfer between the system and surroundings due to macroscopic force acting through a distance and is realized by organized motion of molecules.

For an ***isobaric (constant pressure) process*** integration of the work equation:



$$W = pdV$$

gives $W = p\ (V_2 - V_1)$

Using the equation of ideal gas state for one mol ideal gas:

$$pV = RT$$

allow to obtain the following expression:

$$W = R(T_2 - T_1)$$

Isothermal process (T=const)

$$p = nRT/$$

$$W = nRT\frac{dV}{V}\,.$$

$$W = nRT\int\frac{dV}{V} \text{ and } W = 2.303\ nRT\ lg\frac{V_2}{V_1} \text{ or } W = 2.303\ nRT\ lg\frac{P_1}{P_2}$$

In an ***adiabatic process*** **(q=const)** a gas does not absorb heat from its surroundings

$$W = C_v (T_1 - T_2)$$

For an ***isochoric*** ***(constant volume)*** *process* $dV = 0$, consequently $W = 0$. In this case, a system isn’t able to do expansion work.

The Zeroth Law of thermodynamics

Two systems each of them are found to be in thermal equilibrium with the third system, it is in thermal equilibrium with each of them.

The First law of thermodynamics

- Energy can be neither created nor destroyed and if energy> disappears in one form, it reappears in another form in a strictly equivalent amount.
- It is impossible to construct the first order perpetual-motion machine, i.e. a machine by which ire could obtain work without spending an equivalent amount of energy
- The total energy of an isolated system is constant.

The mathematical expression of the first law of thermodynamics

$$\Delta U = q - W$$

For processes involving only infinitesimally small changes, it is written in the form:

$dU = dq - dW$

__In isochoric process__ $(dV=0)$ the system can not do expansion work, so $dW=0$ and

$dU = dq$

In isochoric process, the heat imparted to the system is spent only to internal energy change.

__In adiabatic process__ $dq=0$, so we can write:

$- dU = dW$

The system is able to do work only at the expense of internal energy.

The mathematical expression of the first law of thermodynamics

In isothermal process, when $T=const$, U is constant too (because U for ideal gas depends only on the T), so $dU=0$ and we can write:

$$dq = dW$$

For isobaric process p=const, so the system is able to do the work of expan-sion and the first law has the following expression:

$$Q_p = (U_2 - U_1) + p(V_2 - V_1) = (U_2 + pV_2) - (U_1 + pV_1) = H_2 - H_1 = \Delta H$$

$$dq = dU + dW \text{ or } dq = dU + pdV = dH$$

Since energy is absorbed or evolved during chemical reactions most frequently in the form of heat, all reactions during which energy is liberated are called **exothermic** ($\Delta H < 0$ or $Q > 0$). Reactions in which energy is absorbed are termed **endothermic** ($\Delta H > 0$ or $Q < 0$).

Enthalpy(H)

Enthalpy(H) is a thermal effect of reaction.

For ideal gases at constant temperature $p\Delta V = \Delta nRT$, so the first law we can write as:

$$\Delta H = \Delta U + \Delta nRT$$

where Δn is the change of moles of the gas during the reaction.

Heat capacity

When the heat flows into the system as a rule the temperature of the system is proportionally increased and we can write, that ***$q=C\Delta T$*.**

$$\mathbf{C = dq/dT}$$

Heat capacity is defined as amount of heat necessary to the change of the tempera-ture of the system in one degree.

Types of capacity:

- ***Specific heat capacity*** is amount of heat necessary for one gram of a matter temperature arising in one degree.
- ***Molar heat capacity*** is amount of heat necessary for one mol of a material temperature arising in one degree.

Heat capacity depends on the temperature and on the conditions under which a process takes place. According to the thermodynamics first law, $dq = dH$ in iso-baric process and $dq = dU$ in isochoric process, hence the ***heat capacity at constant pressure***, $\boldsymbol{Cp}$, is equal to:

$$\boldsymbol{Cp = dH/dT}$$

and ***the heat capacity at constant volume***, $\boldsymbol{Cv}$, is equal to:

$$\boldsymbol{Cv = dU/dT}$$

From the first law $\boldsymbol{dH>dU}$ $\boldsymbol{(dH=dU+pdV)}$**,** consequently $\boldsymbol{Cp>Cv}$, and the difference between them is equal to the work of expansion: $\boldsymbol{Cp - Cv = pdV}$. For ideal gas $\boldsymbol{Cp - Cv = R}$

The Hess's Law

The thermal effect of a reaction depends only on the initial and final conditions of the reacting substances, but not on the intermediate stages of the process.

Consequence of Hess's law

The Hess's Law makes it possible to calculate the thermal effect of the reaction when they cannot be measured directly for some reason of other.

1. The thermal effect of a chemical reaction equals the sum of the formation heats of the resulting substances minus the sum of the formation heats of the reactants.

$$\Delta H^0_{298} = \Sigma \Delta H^o_{f}\text{,products} - \Sigma \Delta H^o_{f}\text{,reactants}$$

$\Delta H^o f$ is in the reference book or tables.

The amount of heat evolved or absorbed during the formation of one mole of a chemical compound from its simple substances is called the heat of formation of the compound.

The formation heat of the simple substances (H_2, Cl_2, O_2 , Na and so on) is equal to 0.0kJ.

2. The thermal effect of a chemical reaction equals the sum of the combustion heat of the reactants minus the sum of the combustion heat of the products.

$$\Delta H^o_{298} = \Sigma\Delta H^o comb,reactants - \Sigma\Delta H^o comb,products$$

The amount of heat evolved during the full combustion of one mole of chemical compound in pure oxygen to burning products is called **the heat of combustion of a compound.**

The combustion heat of the burning products (CO_2, H_2O, HCl and N_2) is equal to 0.0kJ.

3. The heat of formation of a complex substance from simple substances equals its heat of decomposition with the opposite sign.

Kirchhoff’s law

- For the derivative of the reaction enthalpy with respect to the temperature of the reaction we have:

$$\left(\frac{\partial \Delta_r H}{\partial T}\right)_p = \Delta C_p \,,$$

Where

$$\Delta C_p = r\,C_{pm}(\mathrm{R}) + s\,C_{pm}(\mathrm{S}) + \cdots - a\,C_{pm}(\mathrm{A}) - b\,C_{pm}(\mathrm{B}) - \cdots = \sum_{i=1}^{n} \nu_i C_{pmi} \,.$$

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta C_p \, dT \,,$$

This relation is called **Kirchhoff’s law**. It allows us to convert reaction enthalpies from one temperature to another if we know the dependence of the heat capacities of substances on temperature.