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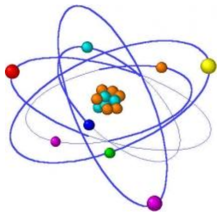
CHEMICAL THERMODYNAMICS

Teaching and methodical manual
for foreign student



Zaporozhye, 2016

ЗАПОРІЗЬКИЙ ДЕРЖАВНИЙ МЕДИЧНИЙ УНІВЕРСИТЕТ

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ХІМІЧНА ТЕРМОДИНАМІКА

Навчально-методичний посібник
для студентів англомовної форми навчання

Запоріжжя, 2016

UDC 544.3(075.8)=111
BBC 24.53я73
C51

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Chemical thermodynamics: teaching and methodical manual for foreign students / A.G. Kaplaushenko, O.R. Pryakhin, B.A. Varinskiy [et al.]. − 2nd ed., updated and suppl. − Zaporozhye, 2016. − 70 p.

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Навчальний посібник розглянуто та затверджено:

Цикловою методичною комісією з фармацевтичних дисциплін
(протокол №__ від ________р.),
Центральною методичною радою ЗДМУ
(протокол №__ від ________р.)

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PREFACE

Medicinal Chemistry is one of the most rapidly developing areas within the discipline of Chemistry, both globally and locally. It is the study of the design, biochemical effects, regulatory and ethical aspects of drugs for the treatment of disease.

The aim of this discipline is to produce graduates with an appropriate background in biology and pharmacology, built upon a strong chemistry foundation.

Methodical recommendation of Medicinal Chemistry is designed to equip students with strong grounding in biological and chemical technique which is relevant to the pharmaceutical world.

The discipline gives an in-depth coverage of the chemical techniques required and relates these to the relevant pharmacology, anatomy, biochemistry and molecular biology.

The whole course of Medical chemistry which consists of ten topics is studied by students-physicians during the first year. Lecturer staff of department has prepared an educational and methodical recommendation in which the theoretical material is stated in the concise and available form.

The distribution of material on each of ten topics that are studied is set according to training program, the thematic plan of lectures and practical training.

The material of each topic is stated in such way that performance of practical work and the solution of situational tasks are preceded by theoretical part in which questions of medicine and biological value and also connection with other disciplines (biological chemistry, normal physiology, pathophysiology and others) are included.

Offered laboratory works and situational tasks will give students the chance to understand theoretical material fully and to use this knowledge in practice.

The experience of teaching medical chemistry shows that it is not always possible to coordinate an order of laboratory works realization with sequence of lecture course statement. That is why students usually have to prepare for practical work performance independently before the lesson. Therefore the theoretical part (in which the necessary volume of knowledge for conscious performance of experiment is given) precedes to each section of these Methodical recommendations.

Increasing of level of seminar and laboratory works is reached by use of such forms of occupations which open and consolidate theoretical knowledge, train scientific thinking, develop creative initiative and impart skills of handling devices and chemicals, chemical ware.

The structures, figures and schemes are clear and easy to follow and color is used well, highlighting main points without being distracting.

Chapters are helpfully signposted throughout, informing the reader how topics are related, which is especially important in such a multidisciplinary subject.

Topics are also presented clearly and with a logical progression culminating in the main points, questions and reading sections at the beginning of each chapter.

An assortment of case studies is provided and the authors work through each one in great detail, giving an overall perspective on the science.

Finally, very useful and informative appendices and a glossary are provided together with a comprehensive index that is good enough to rival any search engine!

There are many books that describe medicinal chemistry and its uses, but these methodological recommendations present medicinal chemistry and its related topics in a clear, informative and interesting way that really demonstrates the application and impact of this fundamental subject in society.

INTRODUCTION

Purpose:

Explore the colorimetric method for determining the thermal effects. Determine the heat of dissolution of salt. Determine the heat formation of crystalline hydrates from anhydrous salt.

Targets:

- Entropy as a Thermodynamic quantity that determine the spontaneity of reactions;
- Relative entropies of substances in different physical states entropy;
- Predicting the sign of entropy changes in chemical reactions;
- Free energy as a Thermodynamic function for spontaneity;
- The calculations of free energy change under standard and nonstandard conditions;
- The relationships between equilibrium constant, K, and ΔG°;
- The use of coupling reactions to drive nonspontaneous reactions.

CONCISE THEORETICAL MATERIAL

1. The First Law of Thermodynamics

Energy is: the ability (or capacity) of a system to do work or supply (or produce) heat.

(1) Kinetic energy is the energy associated with motion; the faster an object moves, the more kinetic energy it has. There is an equation which governs this:

$$K.E. = (1/2)\ mv^2$$

m means mass and v is velocity. This equation means that the general units on kinetic energy are:

$$(\text{mass})\ (\text{distance})^2\ (\text{time})^{-2}$$

Since any mass, time or distance unit could be used, it has been agreed to standardize on specific units for these three quantities and they are the kilogram, second and meter. Inserting them in the above equation gives:

$(\text{kg})\ (\text{m})^2\ (\text{s})^{-2}$

This unit has been given a name: Joule. This is in honor of James Prescott Joule, who in the mid-1800s did pioneering work on energy. The Joule is the standard metric (or SI) unit for all energy.

(2) Potential energy is energy that is stored by virtue of position. There are several different types of storage, of which these four are examples.

(a) Gravitational - this is the most familiar. A rock poised to roll down a hill has potential energy. A ball thrown into the air gains more and more potential energy as it rises. The higher in the gravity field you go, the more potential energy you gain. Generally speaking, chemistry does not concern itself with the potential energy from gravity.

(b) Electrical - in certain materials, you can remove electrons from one area and send them to another. The area losing the electrons becomes more and more positive and the area gaining them becomes negative. The greater and greater the charge difference, the more energy is stored within the system.

(c) Chemical - this is slightly more complex. Certain chemicals have bonds which require little energy to break. This energy must be put into the bond to break it. However, during the course of the chemical reaction, new bonds form which give off MORE energy than that which was put in. Commonly, these reactive compounds are said to "store" energy, but the truth is that the energy released came from a process of first putting in and then getting back more than you put in.

- The positional aspect comes from first breaking bonds between atoms (which takes energy) and then rearranging the atoms in new positions to form new bonds (which gives off energy).
- If you get back more than you put it, this is called exothermic. The net potential energy converted in the reaction shows up as heat, that is the area around the reaction goes up in temperature.
- If you get back less than you put in, this is called endothermic. The increase in potential energy of the newly made compounds is reflected in a heat flow from the surroundings into the chemicals, resulting in a temperature drop in the surroundings.

(d) Nuclear - the famous equation $E = mc^2$ governs this source of potential energy. We can consider the mass itself to be potential energy, since it can be converted from a form not being used (while it is the mass), to kinetic energy. This type of potential energy is released (in measurable amounts) during radioactive decay, fission and fusion.

Work(w)

The usual definition of work is: a force acting over a distance

A more technical definition is: the transfer of energy from one mechanical system to another.

Heat(q)

There is a lot of misunderstanding about what heat is: heat is not a thing, heat is a process.

the definition: heat is the transfer of energy between two objects due to temperature differences.

Notice that the name of the transfer process is heat. What gets transfered is energy. Heat is NOT a substance although it is very convenient to think of it that way. In fact, it used to be thought that heat was a substance.

There is a circular nature to the definitions used:

(a) energy does work or produces heat, but
(b) heat is a transfer of energy.

Ultimately, energy is expressed in the motion of substances. If it is moving, it has energy. If it has the capacity to move, there is some potential energy stored away.

Temperature

The temperature is absolute temperature, measured in Kelvins.

The definition: temperature is a property which is directly proportional to the kinetic energy of the substance under examination.

Another useful definition: temperature is the property which determines the direction heat will flow when two objects are brought into contact.

First Law of Thermodynamics:

- The total amount of energy in the universe is constant.
- The Law of Conservation of Energy is a restatement of the 1st Law of Thermodynamics: Energy is neither created or destroyed in ordinary chemical reactions and physical changes.

Thermodynamic Terms

System: The substances involved in the chemical and physical changes that are being studied.

Surroundings: everything in the systems environment (everything outside the system)

Universe: the system plus its surroundings

Applying the 1st Law of thermodynamics heat can be transferred between the system and its surroundings.

There are two important issues:

1) a great majority of our studies will focus on the change in the amount of energy, not the absolute amount of energy in the system or the surroundings.
2) regarding the direction of energy flow, we have a "sign convention."

Two possibilities exist concerning the flow of energy between system and surroundings:

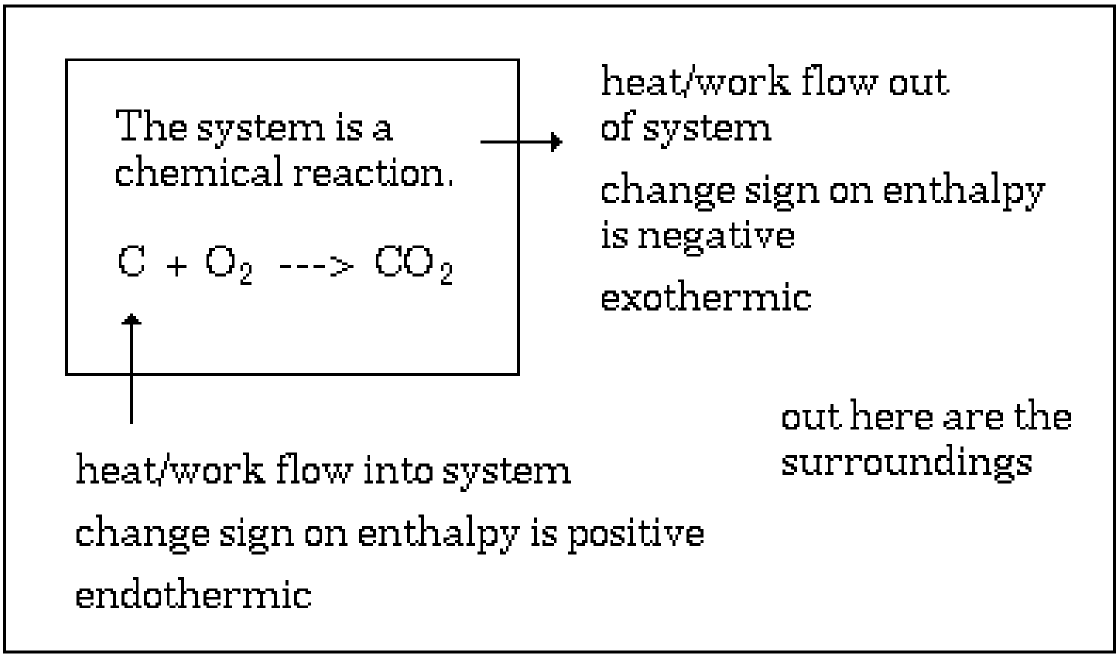
1) The system can have energy added to it, which increases the systems amount of energy and lessens the energy amount in the surroundings.
2) The system can have energy removed from it, thereby lowering its amount and increasing the amount in the surroundings.

We will signify an increase in energy with a positive sign and a loss of energy with a negative sign.

Also, we will take the point-of-view from the system. Consequently:

1) When energy (heat or work) flow out of the system, the system decreases in its amount. This is assigned a negative sign and is called exothermic.
2) When energy (heat or work) flows into the system, the system increases its energy amount. This is assigned a positive sign and is called endothermic.

We do not discuss chemical reactions from the surrounding's point-of-view. Only from the system's.



Thermodynamic State of a System: a defined set of conditions that completely specify all the properties of a system. This normally includes:

- Temperature
- Pressure
- Composition (identity & number of moles of each component)
- Physical state

The properties of a system (P,V,T) are called State Functions.

- State functions only depend on the current state of the system not the path that was used to get to the current state.
- A change in state function describes the difference between the 2 states but not eh process or pathway that was taken
    - For example: if the temperature of a system changes from 273 K to 298 K the system has had a change in state. The temperature change is 25 K, but how the change occurred is not important.

Enthalpy Changes

Remember Enthalpy (H) is energy.

Most chemical and physical changes occur at a constant pressure.

The definition of Enthalpy Change (ΔH) is the quantity of heat transferred into or out of a system as it under goes a chemical or physical change at constant pressure.

$\Delta H = H_{final} - H_{initial}$ or $\Delta H = H_{substances\ produced} - H_{substances\ consumed}$

Enthalpy is a state function. So we may not know the absolute enthalpy (heat content) of a system but it is the change in enthalpy that is useful and can be measured for many processes.

Calorimetry

Calorimetry is an experimental technique used to determine the energy change associated with a chemical or physical process.

- A calorimeter is a device in which an experiment is carried out to determine the energy change of a process. Measuring the temperature change of a known amount of substance with a known specific heat. The change in temperature is caused by the release or absorption of heat by the chemical or physical process being studied.

You will need to be able to complete calorimetry calculations. Examples: page 640 #58,60,62

Thermochemical Equations

Thermochemical Equation: a balanced equation together with its **ΔH** value.

- Examples
  - $C_2H_5OH(l) + 3\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) + 1367\ kJ$

- $C_2H_5OH(l) + 3\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ **ΔH** = -1367 kJ/mol

▪The energy listed in the products or -ΔH indicates that the rxn is exothermic

- $1367\ kJ + 2CO_2(g) + 3H_2O(l) \rightarrow C_2H_5OH(l) + 3\ O_2(g)$
- $2CO_2(g) + 3H_2O(l) \rightarrow C_2H_5OH(l) + 3\ O_2(g)$ **ΔH** = 1367 kJ/mol

▪The energy listed in the reactants or +ΔH indicates that the reaction is endothermic

Remember:

- The coefficients in a balanced thermochemical equation only refer to moles of reactants and products never molecules. So it is okay to write coefficients as fractions when necessary.
- The numerical values of ΔH refer to the number of moles specified by the equation. If a different amount of material is involved then the ΔH must be scaled accordingly.
- The states of all thesubstancesmust be indicated and the ΔHis specific for thestates listed in the equation. Heat is absorbed of released during phase changes so ΔH would change.
- ΔH usually doesn’t change significantly with moderate changes in temp.

Standard States & Standard Enthalpy Changes

The Thermodynamic Standard State of a substance is its most stable pure form under standard pressure (1 atm) and at a specific temperature (usually 25^oC or 298K also known as Room temp).

- Examples: Hydrogen is a gas, mercury is a liquid, sodium is a solid, water is a liquid, and calcium carbonate is a solid.

Standard State Rules:

- For a pure substance in the liquid or solid phase, the standard state is the pure liquid or solid
- For a gas, the standard state is the gas at a pressure of 1 atm, in a mixture of gases, its partial pressure must be 1 atm
- For a substance in solution, the standard state refers to a 1M concentration

The standard enthalpy change, ΔH^{o}_{rxn}, for a reaction refers to the ΔH(change in enthalpy)when the specified amount of reactants are completely converted to the specified amounts of products, all at standard states.

2. Standard Molar Enthalpies of Formation, ΔH^{o}_{f}

Standard Molar Enthalpies of Formation, ΔH^{o}_{f} also known as standard molar heat of formation or just heat of formation

The symbol for the standard molar enthalpy of formation is:

ΔH°_{f}

All chemical reactions involve a change in enthalpy (defined as the heat produced or absorbed during a reaction at constant pressure). The symbol for the change is □H. The subscripted "f" is taken to mean formation when used in the thermochemistry area. The symbol "°" is taken to mean "standard conditions."

Exothermic chemical reactions will have a negative ΔH and endothermic reactions have a positive ΔH. The reason for the sign convention has to do with chemistry's viewpoint of the system and the surroundings.

What this means is that EACH formation reaction has an enthalpy change value associated with it. For example, here is the formation reaction for carbon dioxide:

$C (s) + O_2 (g) \text{--->} CO_2 (g)$

The product(s) have some unknown absolute enthalpy value (call it H_2) and the reactant(s) have another value (also unknown), called H_1. Even though those two values cannot be measured, we can measure the difference (H_2 minus H_1 is called ΔH) in an experiment using a calorimeter.

Definition of Standard Molar Enthalpies of Formation is the enthalpy change for the reaction in which 1 mole of the substance in a specified state is formed form its elements in their standard states.

- The $\Delta H°_f$ value for any element in its standard state is zero.
    - The standard enthalpy of formation for an element in its standard state is ZERO!!!! Elements in their standard state are not formed, they just are. So, $\Delta H°_f$ for C (s, graphite) is zero, but the $\Delta H°_f$ for C (s, diamond) is 2 kJ/mol. That is because graphite is the standard state for carbon, not diamond.

Hess's Law

Law of Heat Summation: the enthalpy change for a reaction is the same whether it occurs in one step or by a series of steps.

Germain Henri Hess, in 1840, discovered a very useful principle which is named for him:

The enthalpy of a given chemical reaction is constant, regardless of the reaction happening in one step or many steps.

Another way to state Hess' Law is:

If a chemical equation can be written as the sum of several other chemical equations, the enthalpy change of the first chemical equation equals the sum of the enthalpy changes of the other chemical equations.

Mathematical representation of Hess's Law:

- $\Delta H^o_{rxn} = \Sigma\ n\ \Delta H°_{fproductss} - \Sigma\ n\ \Delta H\ °_{f\cdot reactantss}$

- Σ = sum of
- n = coefficient from balanced equation

Explanation using several examples:

Example #1

$$\text{C (s, graphite)} \longrightarrow \text{C (s, diamond)} \qquad \Delta H^\circ = ???\ \text{kJ}$$

We need to obtain the enthalpy for this reaction. By the way, notice the presence of the degree sign, °, on the enthalpy. This indicates that the reaction is happening under standard conditions. All reactions will be carried out under standard conditions.

In the common chemistry laboratory, this reaction cannot be examined directly. This is because, regardless of the low enthalpy, the reaction requires a very, very high activation energy to get the reaction started and, in this case, it means both high temperature and high pressure. The consequence is that the enthalpy value cannot be determined directly in almost all labs and, in the ones that can, the process is very, very difficult.

However, Hess' Law offers a way out. If we had two (or more) reactions that could be added together, then we can add the respective enthalpies of the reactions to get what we want. Here are the two reactions we need:

$$\text{C (s, graphite)} + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ = -394\ \text{kJ}$$

$$\text{C (s, diamond)} + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ = -396\ \text{kJ}$$

Reverse the bottom equation. This will put the C (s, diamond) on the product side, where we need it. Then add the two equations together, the oxygen and carbon dioxide will cancel out. This is, of course, what we want since those two substances are not in the final, desired equation. Here are the two equations again, with the second one reversed:

C (s, graphite) + O_2(g) ---> CO_2(g)   ΔH° = -394 kJ

CO_2(g) ---> C (s, diamond) + O_2(g)   ΔH° = +396 kJ

Notice the other change. Look at the enthalpy for the second equation, the one that was reversed. Notice how the sign has changed also. This is an absolute requirement of using Hess' Law - Reversing an equation means reversing the sign on the enthalpy value.

The reason? The first, unreversed equation is exothermic. We know this from the negative in front of the 396. That means that the opposite, reverse equation is endothermic. Putting in enthalpy (endothermic) is the reverse, the opposite of exothermic (giving off enthalpy). Hence, we change the sign EVERY time we reverse an equation.

Now add the equations together. When this is done then add the enthalpies together. Here is the added equation without anything taken out:

CO_2(g) + C (s, graphite) + O_2(g) ---> CO_2(g) + C (s, diamond) + O_2(g)   ΔH° = (-394 kJ) + (+396 kJ)

Notice the items which are the same on both sides and remove them:

C (s, graphite) ---> C (s, diamond) ΔH° = +2 kJ

We now have the answer we desire by using the indirect means of Hess' Law and two relatively easy experiments. Thus we avoid performing a tricky, expensive, possibly dangerous experiment. However, due to Hess' discovery, we know that our indirectly obtained answer is just as valid as if we had done the experiment directly.

Example #2

Calculate the enthapy for the following reaction:

$$N_2(g) + 2O_2(g) \text{ ---> } 2NO_2(g) \quad \Delta H^\circ = \text{??? kJ}$$

Using the following two equations:

$$N_2(g) + O_2(g) \text{ ---> } 2NO(g) \qquad \Delta H^\circ = +180 \text{ kJ}$$

$$2NO_2(g) \text{ ---> } 2NO(g) + O_2(g) \quad \Delta H^\circ = +112 \text{ kJ}$$

In order to solve this, we must reverse at least one equation and it turns out that the second one will require reversal. Here are both with the reversal to the second:

$$N_2(g) + O_2(g) \text{ ---> } 2NO(g) \qquad \Delta H^\circ = +180 \text{ kJ}$$

$$2NO(g) + O_2(g) \text{ ---> } 2NO_2(g) \quad \Delta H^\circ = -112 \text{ kJ}$$

Notice the change for the sign on the enthalpy from positive to negative.

Next, add the two equations together and eliminate identical items. Also add the two enthalpies together.

$$N_2(g) + 2O_2(g) \text{ ---> } 2NO_2(g) \quad \square H^\circ = +68 \text{ kJ}$$

The answer has been obtained: +68 kJ/mol.

Example #3

Calculate ΔH° for this reaction:

$$2N_2(g) + 5O_2(g) \text{ ---> } 2N_2O_5(g)$$

using the following three equations:

$$H_2(g) + (1/2)\ O_2(g) \text{ ---> } H_2O(l) \qquad \Delta H^\circ = -285.8 \text{ kJ}$$

$$N_2O_5(g) + H_2O(l) \text{ ---> } 2HNO_3(l) \qquad \Delta H^\circ = -76.6 \text{ kJ}$$

$$(1/2)\ N_2(g) + (3/2)\ O_2(g) + (1/2)\ H_2(g) \text{ ---> } HNO_3(l) \quad \Delta H^\circ = -174.1 \text{ kJ}$$

This example shows something new not discussed yet. It is obvious that one of the equations with the nitric acid (HNO_3) will have to be reversed. In addition (this is the new part), you will need to multiply through an equation by a particular factor. (In fact, in this equation more than one factor will be needed!!!) The reason for this: to make substances not in the final answer (like the HNO_3) cancel out, there have to be an EQUAL number of them on each side when you add the three equations together.

When you multiply through by the factor, MAKE sure to multiply every component on the reactant side and the product side AS WELL AS . . .
the enthalpy value!!!!!!

Multiply the enthalpy value times the factor and use that new value in the calculation.

One step at a time, but writing all three equations each time. First, focus on the second equation, which is reverse AND multiply through by two:

$$4\ HNO_3(l) \text{ ---> } 2\ N_2O_5(g) + 2\ H_2O(l) \quad \Delta H° = +153.2\ kJ$$

OK, why do you do all that? (1) you need get the N_2O_5 on the right hand side AND (2) need to have it be 2 N_2O_5. Notice that all 4 components (the three substances and the enthalpy) all got doubled. Did you catch the change from negative to positive in the $\Delta H°$?

Now, choose the third equation to work with. Do NOT flip it, but multiply through by four. Why four? First the equation and then the answer:

$$2\ N_2(g) + 6\ O_2(g) + 2\ H_2(g) \text{ ---> } 4\ HNO_3(l) \quad \Delta H° = -696.4\ kJ$$

What does this get you? First, you get the 2 N_2 needed on the left side of the final answer. Second, you get 4 HNO_3 on the right to cancel with the 4 HNO_3 on the left in the second equation.

However, still not at the final answer. To get there, you need to reverse (sometimes "flip" is the verb used) the first equation and multiply through by two.

$2\ H_2O(l) \text{ ---> } 2\ H_2(g) + O_2(g)$ ΔH° = +571.6 kJ

$4\ HNO_3(l) \text{ ---> } 2\ N_2O_5(g) + 2\ H_2O(l)$ ΔH° = +153.2 kJ

$2\ N_2(g) + 6\ O_2(g) + 2\ H_2(g) \text{ ---> } 4\ HNO_3(l)$ ΔH° = -696.4 kJ

The change to the first equation will allow you to (1) cancel out the water, (2) cancel out the hydrogen and (3) cancel out one of the oxygens leaving the five you need for the answer.

The ΔH° for the reaction as written is +28.4 kJ.

One last note: You don't write kJ/mol in this case because of the two in front of the N_2O_5. However, you would need to supply the equation along with the 28.4 value. If you divided through by two, you would get the formation reaction for N_2O_5:

$N_2(g) + (5/2)\ O_2(g) \text{ ---> } N_2O_5(g)$

In this case, you would write $\Delta H°_f$ = 14.2 kJ/mol. The presence of the subscripted "f" indicates that you are dealing with one mole of the target substance.

Example #4

Calculate $\Delta H_f°$ for this reaction:

$6\ C(s) + 6\ H_2(g) + 3\ O_2(g) \text{ ---> } C_6H_{12}O_6(g)$

using the following three equations:

$C(s) + O_2(g) \text{ ---> } CO_2(g)$ ΔH° = -393.51 kJ

$H_2(g) + (1/2)\ O_2(g) \text{ ---> } H_2O(l)$ ΔH° = -285.83 kJ

$C_6H_{12}O_6(s) + 6\ O_2(g) \text{ ---> } 6\ CO_2(g) + 6\ H_2O(l)$ ΔH° = -2803.02 kJ

The answer is -1273.02 kJ/mol.

Bond Energies

Chemical Rxns involve the breaking and making of chemical bonds. Energy is always required to break a chemical bond. Often this energy is supplied as heat.

The bond energy (B.E.) is the amount if energy needed to break 1 mole of bonds in a gaseous covalent substance to form products in the gaseous state at constant temp and pressure.

- The greater the bond energy the more stable (and stronger) the bond is and the harder it is to break. So bond energy is a measure of bond strength.

$\Delta H^o_{rxn} = \Sigma \text{ B.E.}_{reactants} - \Sigma \text{ B.E.}_{products}$ in gas phase rxns only (Remember Σ = sum of)

- Problem solving similar to problems involving heats of formation but instead of $\Delta H°_f$ you use B.E. values. The B.E. values need to be provided.

Changes in Internal Energy, ΔE

Internal Energy, E, is all the energy contained within a specified amount of a substance. It includes:

- Kinetic energy of the molecules
- Energies of attraction and repulsion among subatomic particles, atoms, ion or molecules

Internal Energy is a state function and independent of pathway.

$\Delta E = E_{products} - E_{reactants}$ or $\Delta E = q + w$ (where q = heat and w = work)

ΔE = (amount of heat absorbed by the system) + (amount of work done on the system)

+q = heat absorbed by the system

- q = heat released by the system

+ w = work done on the system

- w = work done by the system

Compression/Expansion are examples of work done on or by a system:

- Expansion (volume increases) – work is done by the system
    - Sign of w is negative
    - ΔV increases and is positive
- Compression (volume decreases) – work is done on the system
    - Sign of w is positive
    - ΔV decreases and is negative

We can substitute $-P\Delta V$ for w in the $\Delta E = q + w$ to get $\Delta E = q - P\Delta V$

Since volume doesn't change much with solids and liquids the $\Delta V = 0$ which means no work is done and then $\Delta E = q$

Relationship Between ΔH &ΔE

$\Delta H = \Delta E + P\Delta V$ (when temp and pressure are held constant)

- Useful for physical changes that involve volume changes (expansion and compression)

$\Delta H = \Delta E + (\Delta n)RT$ (at constant temp and pressure)

$\Delta E = \Delta H - (\Delta n)RT$ (at constant temp and pressure)

- Useful when chemical reactions cause a change in # of moles of gas
- Δn = number of moles gaseous products – number of gaseous moles reactants

Spontaneity of Physical & Chemical Changes

- In a reaction that the formation of products is thermodynamically favored (more stable) is called "product-favored" or spontaneous.
- In a reaction that does not thermodynamically favor the formation of the products is called "reactant-favored" or nonspontaneous.

The concept of spontaneity is very specific in thermodynamics: a spontaneous chemical rxn or physical change is one that can happen without any continuing outside influence.

- Products are favored over reactants
- May occur rapidly, but thermodynamically is not related to speed
- A rxn might be spontaneous but not occur at an observable rate
- Can occur rapidly, moderately or very slowly

The Two Aspects of Spontaneity

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

1. Spontaneity is favored when heat is released during a change (exothermic)
2. Spontaneity is favored when the change causes an increase in disorder

The Second Law of Thermodynamics

Second Law of Thermodynamics: in spontaneous changes the universe tends toward a state of greater disorder.

Entropy, S

Entropy, S, a state function, is a measure of the disorder of the system.

- The greater the disorder of the system the greater the entropy

Entropy of phases:

Gases> Liquids> Solids

Third Law of Thermodynamics: the entropy of a pure, perfect crystalline substance (perfectly ordered) is zero at absolute zero.

The Standard Entropy Change, ΔS^0

- $\Delta S^0_{rxn} = \Sigma nS^0_{products} - \Sigma nS^0_{reactants}$
    - Units of Entropy: J/mol·K

Changes in Entropy can be understood in terms of molecular disorder which allows us to predict the sign of ΔS_{sys}. For example:

- Phase Changes:
    - Melting – particles taken from the ordered crystalline arrangement to a more disordered one where they can slide past one another in the liquid
        - $\Delta S_{sys} > 0$
    - Vaporization or Sublimation – involve a large increase in disorder
        - $\Delta S_{sys} > 0$
    - Freezing, Condensation, & Deposition all involve an increase in order
        - $\Delta S_{sys} < 0$
- Temperature Changes:
    - Temperature Increases – any sample that is warmed the molecules undergo more random motion
        - $\Delta S_{sys} > 0$
- Volume Changes:
    - Volume Increases – when the volume of a sample increases the molecules can occupy more positions; which cause them to be more randomly arranged than when they are closer together in a smaller volume.
        - $\Delta S_{sys} > 0$
    - Volume Decreases – when a sample is compressed and the volume decreases the molecules are more restricted and more ordered.
        - $\Delta S_{sys} < 0$
- Mixing of Substances (even if a chemical rxn doesn’t occur):

    - Mixing Substances – when molecules are more mixed up there is more disorder
        - $\Delta S_{sys} > 0$
        - $NaCl(s) \rightarrow NaCl(aq)$ $\Delta S^0 = +43.1$ J/mol·K
        - $H_2(g) + Cl_2(g) \rightarrow HCl\ (g)$ $\Delta S^0 > 0$
            - b/c on the reactant side the atoms are bonded to identical atoms which is less "mixed up" than the products where unlike atoms are bonded
- Increasing the number of particles:
    - Any process that increases the number of particles increases entropy.
        - $\Delta S_{sys} > 0$
        - $H_2(g) \rightarrow 2H(g)$ $\Delta S^0 = +98.0$ J/mol·K
- Increasing the number of moles of gas
    - Any process that results in an increase the number of moles of gas increases entropy
        - $\Delta S_{sys} > 0$
        - $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ $\Delta S^0 < 0$
            - b/c the reactants contain 3 moles of gas and the products only contains 2 moles of gas

Free Energy Change, ΔG, and Spontaneity

Gibbs Free Energy, G, formulates the relationship between enthalpy and entropy

- $G = H - TS$ (At constant temp and pressure)

Gibbs Free Energy Change, ΔG

- $\Delta G = \Delta H - T\,\Delta S$ (At constant temp and pressure)

The amount by which Gibbs Free Energy decreases is the maximum amount of useful energy that can be obtained to do work.

ΔG is also an indicator of the spontaneity of a reaction or process

- $+\Delta G$ rxn is nonspontaneous (reactants favored)
- $\Delta G = 0$ system is at equilibrium
- $-\Delta G$ rxn is spontaneous (product favored)

ΔG dependent on:

- Temperature and pressure
- States of substances involved
- Concentration if a mixture is involved

The standard state for ΔG_f^0 is 1 atm and a specified temp (usually 25°C)

- Values for ΔG_f^0 are provided in Appendix K along with ΔH_f^0 and S^0 values.
  - For elements in their standard states $\Delta G_f^0 = 0$

The values of ΔG^0 of a rxn can be calculated using the ΔG_f^0 at 298K using the following equation:

$$\Delta G^0_{rxn} = \Sigma\, n\, \Delta G_f^0{}_{products} - \Sigma\, n\, \Delta G_f^0{}_{reactants}$$

Tips For Calculating ΔG^0_{rxn}:

1. Calculating ΔG^0_{rxn} from the values of ΔG^0_f only works if the rxn is at 25°C and 1 atm
2. For calculations involving $\Delta G = \Delta H - T\,\Delta S$ the temperature must be in Kelvins
3. ΔS is usually in Joules (J) and ΔH is usually in kilojoules (kJ) so you must convert one of the units before you combine them in the ΔG equation

The Temperature Dependence of Spontaneity

$\Delta G = \Delta H - T\,\Delta S$ (At constant temp and pressure)		
- ΔH (favored)	+ ΔS (favored)	Rxns are product favored at all temperatures
- ΔH (favored)	- ΔS (unfavored)	Rxns are product favored below a certain temperature
+ ΔH (unfavored)	+ ΔS (favored)	Rxns are product favored above a certain temperatures
+ ΔH (unfavored)	- ΔS (unfavored)	Rxns are reactant favored at all temperatures

QUESTIONS FOR SELF-TRAINING

1. Gibbs Free Energy: Is it Spontaneous? For a certain chemical reaction at standard state conditions, DH^o = -11.4 kJ and DS^o = -117. J/K. What is DG^o in kJ. at 298 K.?
2. Free Energy to K to Pressure at Equilibrium:
3. Consider the following reaction:

$PbCO_3(s)$ <==> $PbO(s) + CO_2(g)$

4. By using the thermodynamic tables, calculate the equilibrium pressure of CO_2 in atm. in the system at 315. ^oC.
5. Free Energy for a Non-Equilibrium System:
6. For the weak acid, nitrous acid, $K_a = 0.00045$ at 298 K. What is the value of DG at 298 K. in kJ. when $[H^+]$ = 0.02500 M., $[NO_2^{1-}]$ = 2.0000e-4 M., and [nitrous acid] = 0.1158 M.
7. Free Energy and Equilibrium Constants:
8. Use data from the thermodynamic tables to calculate K_p at 298 K. for the following reaction:

$2PCl_3(g) + O_2(g)$ --> $2POCl_3(g)$

9. Gibbs Free Energy:
10. A certain reaction has DH^o = 22.0 kJ and DS^o = -48.5 J/K. Calculate DG^o in kJ at 334 K.
11. Trouton's Rule:
12. Most liquids follow Trouton's Rule which says that the enthalpy of vaporization divided by the boiling point (the entropy) is about 88 J/mole-K. If the normal boiling point of ethanol is 78.4 ^{o} C and the enthalpy of vaporization is 38.6 kJ/mol, by what % does the experimental value for the entropy differ from Trouton's Rule? i.e. (experimental - Trouton's Rule)/Trouton's Rule x 100%
13. Free Energy at Different Temperatures:
14. Methanol, CH_3OH, can be made by the reaction of CO with H_2:

$CO(g) + 2H_2(g)$ --> $CH_3OH(g)$

15. Calculate DG^o at 526. K., assuming that DH^o and DS^o do not change with temperature.

16. Temperature at which DG=0:

17. For a particular reaction, DH = -24.2 kJ. and DS = -137. J/K. Assume that DH and DS do not vary with temperature. At what temperature (in Kelvins) will the reaction have DG = 0 ?

18. Free Energy from the Equilibrium Constant:

19. The equilibrium constant for a reaction is 13.9 at a temperature of 479. ^oC. What is the value of DG^o (in kJ/mol) for this reaction?

20. Free Energy of Combustion::

21. Calculate the free energy of combustion in kJ/mol of $C_2H_6(g)$ if all products are brought back to 298 K and 1 atm pressure (i.e. water is formed as a liquid).

TASKS

Exercise #1

Predict whether each of the following reactions has positive or negative entropy change:

(a) $4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$

(b) $Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(l)} + 3CO_{2(g)}$

(c) $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$

Exercise #2

Calculate ΔS^o for each of the following reactions using the standard entropies of the substances involved in each reaction:

(a) $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$

(b) $2C_2H_{6(g)} + 7O_{2(g)} \rightarrow 4CO_{2(g)} + 6H_2O_{(g)}$

Exercise #3

Predict whether the following reaction is spontaneous at all temperature, at high temperature, at low temperature, or not spontaneous under any conditions.

(a) $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$; $\Delta H^o = -198$ kJ

(b) $2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$; $\Delta H^o = -90$ kJ

(c) $N_{2(g)} + 2H_{2(g)} \rightarrow N_2H_{4(l)}$; $\Delta H^o = +51$ kJ

Exercise #4

Calculate $\mathbf{\Delta G^o}$ for the following reactions using $\mathbf{\Delta H^o}$ and $\mathbf{\Delta S^o}$ at 25°C.

(a) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

(b) $4CuO(s) \rightarrow 2Cu_2O(s) + O_2(g)$

(c) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

Exercise #5

Given: $\Delta G^o_f[NH_3]$ = -17 kJ/mol; $\Delta G^o_f[NO]$ = 87 kJ/mol; $\Delta G^o_f[H_2O(g)]$ = -229 kJ/mol, and $\Delta G^o_f[O_2]$ = 0.0 kJ/mol, calculate ΔG^o_{rxn} at 25 ^{o}C for the reaction:

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

Exercise #6

For the reaction: $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$, ΔH^o_{rxn} = 114 kJ and ΔS^o_{rxn} = 146 J/K.

Is the reaction spontaneous at 25^{o}C? Determine the transition temperature that would change the spontaneity of the reaction (either from spontaneous to nonspontaneous or from nonspontaneous to spontaneous).

Exercise #7

For the reaction: $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$, calculate ΔG^o at 250^{o}C using ΔH^o_{rxn} = -90 kJ and ΔS^o = -220 J/K. Is the reaction spontaneous at 250^{o}C? What is ΔG^o at 250^{o}C if the reaction is carried out with P_{CO} = 30 atm, P_{H2} = 60. atm, and P_{CH3OH} = 10. atm.

Exercise #8

For liquid bromine, ΔH^o_{vap} = 29.5 kJ/mol and ΔS^o_{vap} = 89 J/(mol.K). Estimate its boiling point at 1 atm.

Exercise #9

At what pressure would water boils at 25^{o}C? Assume ΔH^o_{vap} = 44 kJ and ΔS^o = 119 J/K

Exercise #10

For the following equilibrium at 425.4 ^oC: $H_2(g) + I_2(g) \rightarrow 2HI(g)$, $\Delta G^o = -25.3$ kJ. What is the equilibrium constant K_p for this reaction at 425.4 ^oC.

Exercise #11

The reaction: $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$, is an endothermic reaction ($\Delta H^o > 0$) and has $K_p = 11.5$ at 600 K. Calculate ΔG^o at 600 K. How would you predict the magnitude of K_p at 25^oC compared to that at 600 K? Explain your reasoning.

Exercise #12

Calculate ΔG^o for the reaction: $Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(s) + Al_2O_3(s)$

If $2Fe(s) + {}^3/_2\, O_2(g) \rightarrow Fe_2O_3(s)$; $\Delta G^o = -740$ kJ

and $2Al(s) + {}^3/_2\, O_2(g) \rightarrow Al_2O_3(s)$; $\Delta G^o = -1582$ kJ

Exercise #13

Adenosine triphosphate (ATP) is essential for muscle contraction, protein building, nerve conduction, and numerous other energy-requiring processes in the body. These nonspontaneous processes are coupled to the spontaneous hydrolysis of ATP to ADP. In a similar manner, ATP is regenerated by coupling its formation to other energy-releasing reactions, one of which is

Creatine-phosphate → creatine + phosphate $\Delta G^o = -43$ kJ/mol

ADP + phosphate → ATP ; $\Delta G^o = +30$ kJ/mol

Calculate ΔG^o for the overall reaction:

Creatine-phosphate + ADP → creatine + ATP

THE STANDARD ANSWERS

Example #1

$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$, (□$n_p$ > □n_r)

$\Delta S^o_{reaction} = \{(3 \text{ x } S^o_{CO2}) + (4 \text{ x } S^o_{H2O})\} – \{(S^o_{C3H8}) + (5 \text{ x } S^o_{O2})\}$

$= \{(3 \text{ x } 214 \text{ J/K}) + (4 \text{ x } 189 \text{ J/K})\} – \{(270 \text{ J/K}) + (5 \text{ x } 205 \text{ J/K})$

$= (642 \text{ J/K} + 756 \text{ J/K}) – (270 \text{ J/K} + 1025 \text{ J/K}) = 103 \text{ J/K}$

Example #2

$CO_{(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(g)}$, $(\Delta n_p < \Delta n_r)$

$\Delta S^o_{reaction} = (S^o_{CH3OH}) – \{(S^o_{CO}) + (2 \text{ x } S^o_{H2})\}$

$= 240 \text{ J/K} – \{198 \text{ J/K} + (2 \text{ x } 131 \text{ J/K}) = 240 \text{ J/K} – 460 \text{ J/K} = -220 \text{ J/K}$

For reactions that have the same total number of gaseous substances is the same on both side of the equations, the entropy change (increase or decrease) is difficult to predict without doing actual calculations. For these reactions ΔS will be relatively small. For example, we cannot predict whether the entropy increases or decreases in the following reaction:

$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$,

(Calculation of entropy change yields $\Delta S^o = 20$ J/K at 25 ^oC)

Example #3

Consider the reaction: $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$,

with $\Delta H^o = -92$ kJ and $\Delta S^o = -199 \text{ J/K} = -0.199 \text{ kJ/K}$

At 25 ^oC, $T\Delta S^o = 298 \text{ K x } (-0.199 \text{ J/K}) = -59.3 \text{ kJ}$

$\Delta G^o = \Delta H^o - T\Delta S^o = -92 \text{ kJ} – (-59.3 \text{ kJ}) = -33 \text{ kJ}$;

➔ reaction is spontaneous at 25 ^oC

At 200 ^oC, $T\Delta S^o = 473 \text{ K x } (-0.199 \text{ J/K}) = -94.1 \text{ kJ}$;

$\Delta G^o = \Delta H^o - T\Delta S^o = -92 \text{ kJ} – (-94.1 \text{ kJ}) = 2 \text{ kJ}$;

➔ reaction is nonspontaneous at 250^oC

Example #4

Consider the reaction: $CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)}$,

with $\Delta H^o = 206$ kJ and $\Delta S^o = 216$ J/K = 0.216 kJ/K

At 25 °C, $T\Delta S^o = 298 \text{ K} \times (0.216 \text{ J/K}) = 64.4$ kJ

$\Delta G^o = \Delta H^o - T\Delta S^o = 206 \text{ kJ} – 64.4 \text{ kJ} = 142$ kJ;

➔ reaction is nonspontaneous at 25°C.

At 900°C, $T\Delta S^o = 1173 \text{ K} \times (0.216 \text{ J/K}) = 253$ kJ;

$\Delta G^o = \Delta H^o - T\Delta S^o = 206 \text{ kJ} – 253 \text{ kJ}) = -47$ kJ;

➔ reaction is spontaneous at 900°C

EXPERIMENTAL PART

Laboratory work: The determination of heat hydrate

Work is carried out in the calorimeter.

Experiment is done in two stages.

Experiment 1.

1. Weigh 5 g KNO_3 up to 0.01 g.

2. In Dewar flask (vacuum flask) pour 300 ml distilled water to determine, put thermometer and mixer in, determine the temperature for 5 min every 30 sec.

3. Add weighted KNO_3 to water in Dewar flask and quickly close the vessel, make temperature measurements again for 5 min. every 30 sec. Watch the thermocline (temperature jump).

4. Construct a graph of temperature versus time.

5. Determine the change in temperature graphically.

6. Calculate the calorimeter constant, assuming that the thermal effect of the dissolution is ΔH_{KNO3} = 35,62 kJ/mol or (8,4 kcal/mol), according to equation:

$$C\kappa = \frac{\Delta H \cdot g}{M \cdot \Delta t} - 0,3$$

where C_κ- stationary temperature,

ΔH - heat of solution (35,62 kJ/mol or 8,4 kcal/mol);

g - sample, g;

M - molecular weight KNO_3;

Δt – the search results of the temperature change by graph;

0,3 – sample of water, кг.

Experiment 2. Determination of heat of hydrate formation.

1. Weigh $CuSO_4{\cdot}5H_2O$ (sample) in an amount of 8 g up to 0,01 g.

2. In Dewar flask (vacuum flask) pour 300 ml distilled water to determine, put thermometer and mixer in, determine the temperature for 5 min every 30 sec.

3. Add weighted sample to water in Dewar flask, make temperature measurements for 5 min. every 30 sec. Watch the thermocline (temperature jump).

4. Draw the graph coordinates in a time-temperature and find Δt.

5. Determine the heat effect of dissolving salt of $CuSO_4 \cdot 5H_2O$ using formula:

$$\Delta H_2 = \frac{(0{,}3 + C_к)M\Delta t}{g}$$

Legend match with formula of experiment 1.

6. Take a sample of the anhydrous salt $CuSO_4 \cdot 5H_2O$ in an amount of 5 g up to 0.01 g and repeat the stages 2, 3, 4, 5 in paragraphs of this section (ΔH_1).

7. Determine the heat formation of crystalline hydrates by thermal effects which were found in stages 5 and 6 according to Hess's Law.

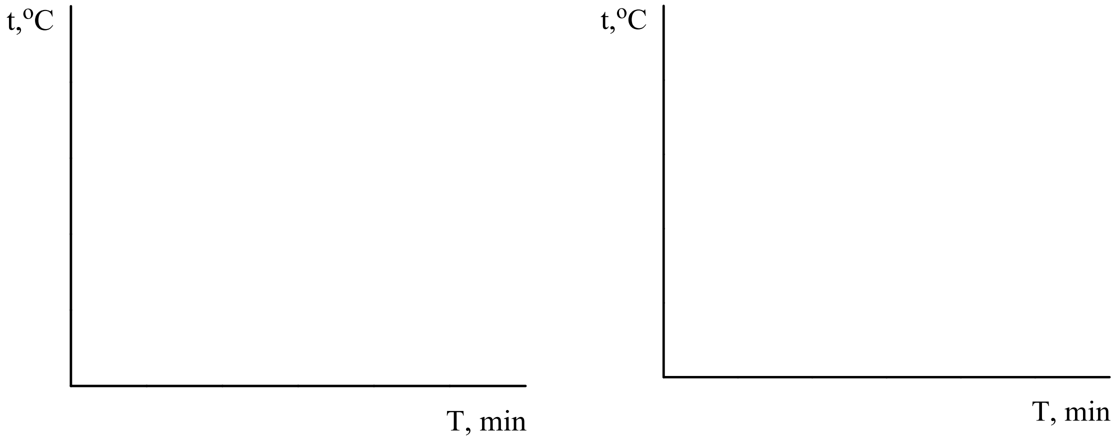
$$\Delta H_3 = \Delta H_1 - \Delta H_2 \text{, where}$$

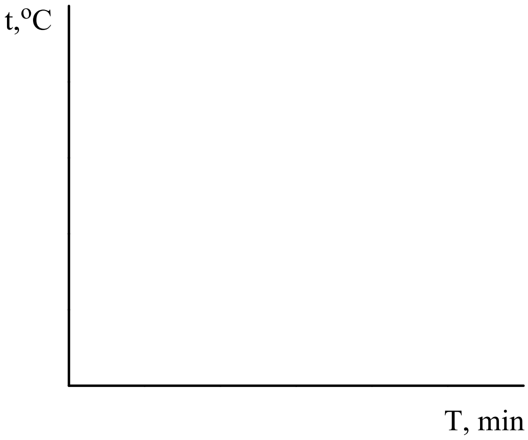
ΔH_1 - heat of solution of the anhydrous salt,

ΔH_2 - heat of solution of hydrated $CuSO_4 \cdot 5H_2O$,

ΔH_3 – heat of formation hydrates you need to search (ΔH can be expressed in kcal/mol or kJ/mol).

Graphical determination of the temperature change





$Cк=$

$\Delta H_1=$

$\Delta H_2=$

$\Delta H_3=$

TESTS

The influence of temperature on an equilibrium constant expresed by an equation of the reaction isobar: d ln K/dT = dH/RT*RT. To what side the equal balance will be shifted, if dH is negative?

a) *To the side of source substances;
b) To the side of products;
c) The equal balance will not be shifted.

Select an exact record of an equation of an isotherm of chemical reaction:

a) *dG =-RT lnKp;
b) dG =RT lnKp;
c) dF=RT ln P;
d) dS=K ln W.

What equation it is possible to evaluate temperature effect on an equilibrium constant by?

a) *By an equation of the reaction isobar;
b) By an equation of Vant-Hoff;
c) By an equation of the reaction isotherm;
d) By an equation of Bolzman.

Select valid conditions dislodging equal balances of reacting $3H_2+N_2=2NH_3$-dH to the side of formation of a product:

a) *Decrease of temperature and increase of pressure;
b) Increase of temperature and increase of pressure;
c) Increase of temperature and decrease of pressure;
d) Decrease of temperature and decrease of pressure.

Enthalpy factor has the sign “-”, and entropy has sign “+”. What are direction and condition of process?

a) *The reaction goes at any temperature;

b) The reaction can go only at a heat;
c) The reaction does not go in general;
d) The reaction goes at low temperature.

Enthalpy factor is positive, and entropy is negative. What are direction and conditions of process?

a) *The reaction does not go in general;
b) The reacting can go only at a heat;
c) The reaction goes at any temperature;
d) The reacting goes at low temperature.

Enthalpy and the entropy factors have the sign “-”. What are direction and conditions of process?

a) *The reaction goes at low temperature;
b) The reaction can go only at a heat;
c) The reaction does not go in general;
d) The reaction goes at any temperature.

The system is in equal balance. Thus:

a) *$dG=0$;
b) $dG> 0$;
c) $dG< 0$.

For chemical reaction, that is spontaneously flowing in a forward direction is characteristic:

a) *$dG< 0$;
b) $dG> 0$;
c) $dG=0$.

Whether the statement, that the energy of the Gibbs is equal to the algebraic sum of entropy and enthalpy factors is correct?

a) *Yes;
b) No.

Enthalpy and the entropy factors have the sign “+”. What are direction and conditions of process?

a) *The reaction can go only at heats;
b) The reaction does not go in general;
c) The reaction goes at any temperature;
d) The reaction goes at low temperatures.

For spontaneously flowing processes entropy is:

a) *More than zero point;
b) Equal to zero point;
c) Less than zero point;
d) Is a constant.

For the insulated system at a reversible process dS:

a) *Is equal to zero point;
b) Is greater than zero point;
c) It is less than zero point.

Does the statement that the second law of thermodynamics on the basis of variation of entropy enables to judge probability of weep of process is correct?

a) *Yes;
b) No.

The system is in isochoric-isothermal conditions. What state function we must use for its description?

a) *Energy of the Helmholtz;
b) Energy of the Gibbs;
c) Bound energy;
d) Enthalpy;
e) Entropy.

The system is in isobaric-isothermal balance. What function we must select for the description of process?

a) *Energy of the Gibbs;
b) Entropy;
c) Enthalpy;
d) Energy of the Helmholtz;
e) Intrinsic energy.

Select a valid equation for energy of the Helmholtz:

a) *dF=dU-TdS;
b) A=TdS-dU;
c) dG=dH-TdS;
d) dF=dU+TdS;
e) A=dG.

Select a valid equation for energy of the Gibbs:

a) *dG=dH-TdS.
b) dF=dU+TdS;
c) dG=dH+TdS;
d) dF=dU-TdS.

Work of a reversible process in comparison to work of an irreversible process always is:

a) *More;

b) Less;
c) They are identical.

Select a valid equation of the second beginning of a thermodynamics:
a) *dS=dQ/T;
b) dG=dH-TdS;
c) A = -dG;
d) S=K ln W.

For what persistence of conditions energy of the Helmholtz is used?
a) *VT;
b) V;
c) PT;
d) SV;
e) P

For what persistence of conditions is used energy of the Gibbs?
a) *PT;
b) T;
c) P;
d) V;
e) SV.

Whether the following statement is correct: “With growth of a randomness of a system the entropy is descending”?
a) *No.
b) Yes

What equation entropy and state probability of a system are connected by?
a) *Bolzman;

b) Hess;
c) Vant-Hoff;
d) Kirhhoff.

What is the nature of the second beginning of a thermodynamics?

a) *Relative;
b) Absolute.

At what temperature the third beginning of a thermodynamics will be realized?

a) *0 K;
b) 298 K;
c) 273 K;

Entropy of an ideal crystal matter at absolute zero is:

a) *Equal to zero point.
b) More than zero point;
c) Less than zero point;
d) It is not meaningful;

Whether it is possible to calculate an absolute value of entropy?

a) *Yes;
b) No.

For what thermodynamic systems the entropy is a criteria of a possibility of weep of process?

a) *Insulated.
b) Open;
c) Closed;

Select a valid ratio for “bound” energy:

a) *TdS;
b) dQ/T;
c) dQ/P;
d) SdT;
e) dF.

Select a proper correlation:

a) *dS=dQ/T;
b) dS=dH*T;
c) dS=dH/RT*RT;
d) dS=dQ/dT;

Select a valid ratio for a “normalized” heat:

a) *dQ/T;
b) TdS;
c) dQp;
d) dG;
e) dF.

To characterize a bound energy following concepts are used:

a) *Entropy;
b) Enthalpy;
c) Energy of the Gibbs.

Whether the following statement is correct: “The process is called thermodynamically convertible, when it can be realized in direct and reverse direction without variations in an environment”?

a) *Yes;
b) No.

Conception of entropy in thermodynamics has entered by:

a) *Klausius;
b) Joule;
c) Thompson;
d) Hess;
e) Arrhenius.

The dependence of heat effect on temperature express by an equation of:

a) *Kirhhoff;
b) Hess;
c) Bolzman;
d) Vant-Hoff;
e) Arrhenius.

Heat effect of chemical reaction:

a) *Depends on temperature;
b) Does not depend on temperature;
c) Depends on some reactionsonly.

Variations of heat effect with temperature is equal to a differential:

a) *Calorific capacities.
b) Energy of Gibbs;
c) Enthalpies;
d) Entropies;

The first law of thermodynamics allows:

a) *To evaluate the power performances of process;
b) To determine a possibility of weep of process;
c) To determine directions of process;
d) To calculate equilibrium state of a system.

Whether the verbiage is valid: “The heat cannot of itself pass from a cold body to ardent”?

a) *Yes;
b) No.

Whether the statements are equivalent: 1. The heat cannot of itself pass from a cold body to ardent, not keeping variations in an environment. 2. The different kinds of energy have a tendention to turn to a heat, and heat to be dispersed, i.e. it is impossible completely to turn the heat into work.

a) *Yes;
b) No.

In homologous sequences the heat of combustion is increased with each CH2-group on:

a) *660 J;
b) 101 J;
c) 213 J;
d) 728 J;
e) 54 J.

The heat effect of a neutralization reaction in sequence of acids HCl, HNO3, H2SO4 will be:

a) *Remain a constant.
b) To ascend;
c) To descend;

Heat effect of a neutralization reaction of acids of different force is:

a) *Constant;
b) Depends on their basicity;

c) Is determined by oxidizing operating.

The heat effect of a neutralization of a strong acid is equal:

a) *-57.3 kJ;
b) -68.5 kJ;
c) 660 J;
d) 0 kJ;
e) 1385 kJ;

The persistence of significances of heat of neutralization for any pair of a strong acid and strong alkali is correctly explained by the theory of:

a) *Arrhenius;
b) Vant-Hoff;
c) Lengmure;
d) Mendeleyev;
e) Hess.

The heat of dilution is called:

a) *Heat effect of dissolution 1 mole of matter in very large volume of resolvent;
b) Heat effect of dissolution of matter;
c) Heat effect of dissolution of 1 mole of matter;
d) Heat effect of dissolution of 1 mole of matter in standard conditions.

What is the heat effect of reaction, if conditionally 2AB + 2CD = 2ABCD of heat of forming AB=5 KJ, CD=10 KJ, ABCD=20 KJ?

a) *10 KJ;
b) -10 KJ;
c) 70 KJ;
d) 20 KJ;

e) 50 KJ.

For reaction of combustion of acetylene the heats of forming of source substances and products are given. What consequent from the law of Hess you will use for accounting of heat effect of reacting?

a) *First;
b) Second;
c) Not any of them.

Standard heat of combustion is:

a) *Heat effect of oxidizing reaction of 1 mole of matter up to higher oxides;
b) Heat effect of oxidizing reaction of 1 mole of matter in standard conditions.

Enthalpy of formation of simple matter:

a) *Is equal to zero point.
b) It is more than zero point;
c) It is less than zero point.

Whether the enthalpies of water formation in liquid and vaporized state are identical?

a) *No;
b) Yes.

It is more, less or the identical amount is of heat is produced at formation of 1 mole of steam in comparison to 1 mole of pool water?

a) *It is less.
b) It is more;
c) Identical amount;

Whether the verbiage is valid: “The enthalpy of formation is a heat effect of formation of combination in standard conditions”?

a) *No.
b) Yes;

Whether will be executed the law of the Hess in conditions of constant pressure Qp=dH?

a) *Yes.
b) No;

Select valid standard conditions:

a) *101.3 ePa, 298 E.
b) 100 ePa, 298 K;
c) 100 ePa, 273 K;
d) 101.3 ePa, 273 K;

Whether will be executed the law of the Hess in conditions of constant volume Qv=dU?

a) *Yes;
b) No.

For what persistence of conditions the law of Hess is valid?

a) *P, V;
b) P, T;
c) P, S;
d) V, m;
e) S, T.

The basic law of thermochemistry was formulated:

a) *By Hess;
b) By Vant Hoff;
c) By Lomonosov;
d) By Joule;
e) By Arrhenius.

Whether the verbiage of the law of Hess is valid: “The heat effects of chemical reactions depend only on the nature both state of source substances and final products and do not depend on intermediate reactions”?

a) *No.
b) Yes;

For isovolumic process expansion work:

a) *Is equal to zero point;
b) Is maximal;
c) Is a constant and is always determined by pressure;
d) Depends on temperature of process.

For a condition V=const heat effect:

a) *Is equal to variation dU;
b) Is equal to zero point;
c) Is equal to variation of enthalpy of process;
d) Is equal to work of process;

For isobaric process heat effect:

a) *Is equal to variation dH.
b) Is always maximal;
c) Is equal to zero point;
d) Is equal to variation dU;

Enthalpy:

a) *Depends only on initial and final parameters;
b) Depends on paths of weep of process;
c) Is not the state function of a system;
d) Is a measure of a randomness of a system.

Select an exact equation:

a) *dH=dU+pdV;
b) dH=dU-pdV;
c) dU=dH+pdV;
d) dH=dU+SdT;

Select exact expression for Qp:

a) *Qp=dU+pdV;
b) Qp=dU;
c) Qp=dS+pdV;
d) Qp=Qv-pdV.

Work and heat of process:

a) *In definite cases the heat does not depends on paths of weep of process;
b) Always depends on paths of weep of process;
c) As intrinsic energy and enthalpy do not depend on paths of weep of process;

If the reaction goes with separation of a heat, then:

a) *Its enthalpy is decreased;
b) Its enthalpy is increased;
c) The enthalpy is not changed, since it is a constant.

Heat effect of an isochoric and isobaric process:

a) *Does not depend on paths of weep;
b) Depends on conditions of weep;
c) Depends on paths for isobaric, but does not depend for isochoric;
d) Depends for isochoric, but does not depend for isobaric;
e) Is a constant always.

Heat:

a) *Only of isochoric and isobaric processes is a heat effect.
b) Always is a heat effect of process;
c) Is a heat effect of the isochoric process, but not of isobaric;
d) Isochoric and isobaric processes are not heat effects;

The verbiage of the first beginning of thermodynamics:

a) *The heat is spent for variation of intrinsic energy and undertaking of work;
b) The heat is spent for separation of intrinsic energy and undertaking of work;
c) The intrinsic energy of a system is equal to the sum of produced heat and undertaking work.

Intrinsic energy of the insulated system:

a) *A constant magnitude;
b) Is equal to zero point;
c) Increases in isothermal processes;
d) Descends at adiabatic compression.

If the stock of intrinsic energy of a system is decreased, then:

a) *The quantity of heat is decreased, and the work a is undertaking by the system;

b) The quantity of heat is increased, and the work is undertaking by the system;
c) The quantity of heat is increased, and the work is undertaking over the system.

Absolute value of intrinsic energy:

a) *It is impossible to determine;
b) It is possible to determine;
c) It is possible to determine only in a number of cases.

The first law of thermodynamics is:

a) *A special case of a law of saving of energy, bounded with its transition into a heat and work;
b) The law of saving of a matter;
c) The law of saving of matter and energy;
d) A special case of a law of saving of energy, bounded with its transition from one kind in other.

Select an exact record of an equation of the first beginning of thermodynamics:

a) *dQ=dU+dA;
b) dU=dQ+dA;
c) dA=dQ+dU.

The heat is:

a) *A quantitative measure of transition of different kinds of energy;
b) Energy contracted in a system;
c) A measure of intrinsic energy of a system;
d) Energy of movement of microparticles of a system.

Intrinsic energy:

a) *Is the state function of a system;
b) Is not the state function of a system;
c) Depends on paths of transition of a system from one state into other;
d) Does not depend from initial and final state of a system.

The phase is:

a) *A part of a system with the identical chemical and thermodynamic properties which have been carved out from other parts;
b) Individual chemical agent;
c) A definite succession of process;
d) A part of a system with different chemical, but identical thermodynamic properties;
e) A piece of the system which have been carved out with division surface from an environment.

The intrinsic energy is:

a) *Full margin of energy of a systems which not includes potential and kinetic energy;
b) Energy of heat motion of particles of a system;
c) Magnitude describing quantitative transition of a heat into work.

The thermodynamic operation is:

a) *A quantitative measure of transition of different kinds of energy from one to another;
b) Always – product of multiplication of the pressure on the volume;
c) A measure of intrinsic energy of a system;
d) An amount of energy, transiting into the heat and work;

In a state of thermodynamic equilibrium thermodynamic parameters:

a) *Are not changed spontaneously and the constant values are unchanged; Are equal to zero point;
b) The maximum ratings reach;
c) Are not changed spontaneously and have different values in different phases.

The heterogeneous system is:

a) *A system composed of several phases;
b) A multicomponent system;
c) A system composed of two and more matters;
d) A system composed of components, carved out from each other;
e) A system composed of two and more components in different phases.

The homogeneous system consists of:

a) *Components were in one phase;
b) Homogeneous phases;
c) Homogeneous components;
d) Homogeneous components in different phases;
e) Homogeneous components in homogeneous phases.

The open system is:

a) *A system exchanging energy with an environment and mass;
b) A system, in which the exchange reactions with an environment flows;
c) A system exchanging matter with an environment;
d) A system, to which the access is open from the side of an environment.

Living organisms are:

a) *Systems exchanging energy and mass with an environment;
b) The insulated thermodynamic systems;
c) The closed systems;

d) Systems carved out from an environments and which are not exchanging matter with it;

The chemical thermodynamics studies:

a) *Heat effects, directions and equal balance of chemical processes;
b) Dodges of weep of reactions;
c) Speed of chemical reactions and equal balance.

The chemical thermodynamics bases:

a) *On three basic laws (beginnings);
b) On the different laws and equations of physics;
c) On two basic laws (beginnings);
d) On five basic laws (beginnings).

The thermodynamic system is:

a) *Collection of the material objects which have been carved out from an environment;
b) Definite succession of joint of the constituents;
c) The device permitting to convert a heat into work;
d) Collection of material and incorporeal objects;
e) Collection of material objects and environment;

Depending on nature of interplay with an environment the thermodynamic systems are divided on:

a) *Insulated, open and closed;
b) One, two, three-component;
c) Homogeneous and heterogeneous;
d) Exogenic and endogenic;
e) Balanced and unbalanced.

The insulated system is:

a) *A system which is not exchanging matter, nor energy with an environment;
b) A system which has been carved out from an environment;
c) A system which is not exchanging matter with an environment;
d) A system which is not exchanging a heat with an environment;

The closed system is:

a) *A system exchanging with an environment only energy;
b) A system, insulated from an environment;
c) A system which is not exchanging heat, nor work with an environment;
d) A system which is not exchanging energy and matter with an environment;

The chemical thermodynamics is a branch of science learning:

a) *Interconversions of a heat and work;
b) Methods of transition of a heat from one body to another;
c) Interconversions of different kinds of energy;
d) Transformations of different kinds of energy in the form of a heat and work.

The influence of temperature on an equilibrium constant expresed by an equation of the reaction isobar: d ln K/dT = dH/RT*RT. To what side the equal balance will be shifted, if dH is negative?

a) *To the side of source substances;
b) To the side of products;
c) The equal balance will not be shifted.

Enthalpy and the entropy factors have the sign “+”. What are direction and conditions of process?

a) *The reaction can go only at heats;
b) The reaction does not go in general;
c) The reaction goes at any temperature;
d) The reaction goes at low temperatures.

For spontaneously flowing processes entropy is:

a) *More than zero point;
b) Equal to zero point;
c) Less than zero point;
d) Is a constant.

Select an exact record of an equation of an isotherm of chemical reaction:

a) *$dG =-RT \ln Kp$;
b) $dG =RT \ln Kp$;
c) $dF=RT \ln P$;
d) $dS=K \ln W$.

What equation it is possible to evaluate temperature effect on an equilibrium constant by?

a) *By an equation of the reaction isobar;
b) By an equation of Vant-Hoff;
c) By an equation of the reaction isotherm;
d) By an equation of Bolzman.

Select valid conditions dislodging equal balances of reacting $3H_2+N_2=2NH_3-dH$ to the side of formation of a product:

a) *Decrease of temperature and increase of pressure;
b) Increase of temperature and increase of pressure;
c) Increase of temperature and decrease of pressure;

d) Decrease of temperature and decrease of pressure.

Enthalpy factor has the sign “-”, and entropy has sign “+”. What are direction and condition of process?

a) *The reaction goes at any temperature;
b) The reaction can go only at a heat;
c) The reaction does not go in general;
d) The reaction goes at low temperature.

Enthalpy factor is positive, and entropy is negative. What are direction and conditions of process?

a) *The reaction does not go in general;
b) The reacting can go only at a heat;
c) The reaction goes at any temperature;
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Heat effect of chemical reaction:

a) *Depends on temperature;
b) Does not depend on temperature;
c) Depends on some reactionsonly.

For the insulated system at a reversible process dS:

a) *Is equal to zero point;
b) Is greater than zero point;

The system is in isochoric-isothermal conditions. What state function we must use for its description?

a) *Energy of the Helmholtz;
b) Energy of the Gibbs;
c) Bound energy;
d) Enthalpy;
e) Entropy.

The system is in isobaric-isothermal balance. What function we must select for the description of process?

a) *Energy of the Gibbs;
b) Entropy;
c) Enthalpy;
d) Energy of the Helmholtz;
e) Intrinsic energy.

Work of a reversible process in comparison to work of an irreversible process always is:

a) *More;
b) Less;
c) They are identical.

Entropy of an ideal crystal matter at absolute zero is:

a) *Equal to zero point.
b) More than zero point;
c) Less than zero point;
d) It is not meaningful;

For what thermodynamic systems the entropy is a criteria of a possibility of weep of process?

a) *Insulated.
b) Open;
c) Closed;

Select a valid ratio for “bound” energy:

a) *TdS;
b) dQ/T;
c) dQ/P;
d) SdT;
e) dF.

Select a valid ratio for a “normalized” heat:

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b) TdS;
c) dQp;

d) dG;
e) dF.

Select a proper correlation:

a) *dS=dQ/T;
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a) *It is less.
b) It is more;
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The verbiage of the first beginning of thermodynamics:

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