

The Gibbs Function of a Chemical Reaction*

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RECEIVED SEPTEMBER 12, 2007; REVISED OCTOBER 12, 2007; ACCEPTED OCTOBER 17, 2007

Keywords
extent of reaction
Gibbs function
reaction quantities
chemical equilibrium
degree of reaction

By defining the extent of reaction as the amount of chemical reactions (moles of reactions) as given by the reaction equation the stoichiometric number of a species taking part in the reaction can be defined as the change in the amount of the species with the extent of reaction. The change in the Gibbs function with the advancement is analyzed in detail for a system of reacting ideal gases at constant temperature and pressure. The changes are split into three contributions: the standard Gibbs function of the reaction, the pressure correction for cases when the total pressure differs from the standard value and the contribution of mixing. The first two contributions depend linearly on the extent of reaction and the third is the only one causing the Gibbs function to have a minimum between the minimum and maximum extent, or at a degree of reaction between 0 and 1. The most convenient way to describe such processes is by plotting the change in the Gibbs function divided by the maximum extent of reaction as a function of the degree of reaction, where both axes represent intensive quantities. Such a plot does not depend on the size of the system but only on the temperature, pressure, ratio of initial amounts and the nature of the reaction. A spread-sheet program (MS Excel) depicting the variation of the Gibbs function with the degree of reaction for given input data is provided separately as supplementary material available via the Internet.

INTRODUCTION

In ideal systems where there are no interactions between molecules or in systems where such interactions are negligible the energy is a linear function of the amounts of species in the system. Thus, if a chemical process takes place and consequently the amounts of reactants and products change the energy of the system will change linearly with the quantity describing the progress of the reaction and which is linearly dependent on the amounts of reacting species. This is not so with the entropy, a function which in addition to a linear dependence also has a contribution owing to the mixing of the species taking part in the reaction.

Chemical thermodynamics teaches us that the equilibrium is the state of maximum entropy of the universe: the studied system and its surroundings. In order to focus on the system only, another state function was introduced: the Gibbs function or the Gibbs energy often still called free energy. Its minimum defines the state of equilibrium and is therefore of crucial importance in examining chemical equilibria. The variation of the Gibbs function with the advancement of a chemical reaction is described in numerous secondary school textbooks, texts on General Chemistry, as well as in Physical Chemistry texts. Yet there are only few texts which describe the variation of the Gibbs function with the progress of the reaction in a satisfactory way.

* Dedicated to Professor Nikola Kallay on the occasion of his 65th birthday.

THE EXTENT OF REACTION CONCEPT

The quantity uniquely describing the advancement of a chemical reaction is usually termed the extent of reaction, or rarely the advancement, and has the recommended symbol¹ ξ . Kondepudi and Prigogine² describe it as a state variable of a chemical system. It can be defined simply as the chemical amount (formerly called the number of moles) of transformations indicated by the reaction equation.³ If we denote the number of such reaction events by N_r , then the extent of reaction or chemical amount of transformations (moles of reactions) is simply

$$\xi = \frac{N_r}{L} \quad (1)$$

where L is the Avogadro constant. Conceptually, this definition is straight-forward, however, it does not provide a simple method of determining the value of the extent of reaction. This is probably the reason why it is usually avoided and international recommendations^{1,4} as well as most textbooks^{5,6} define the extent of reaction in a practical way in terms of the change in the amount of a reactant or a reaction product, n_B ,

$$\Delta \xi = \frac{\Delta n_B}{\nu_B} \quad (2)$$

where ν_B denotes the stoichiometric number (negative for reactants and positive for products). This practical definition, however, often hides the true meaning of the concept and it is sometimes confused with the dimensionless degree of reaction¹

$$\alpha = \frac{\xi}{\xi_{\max}} \quad (3)$$

where ξ_{\max} is the maximum extent of reaction when at least one reactant, the limiting reactant, is exhausted. If the initial amount of a reactant is denoted by $n_{R,0}$, the change at the stage when it is exhausted is obviously $\Delta n_R = -n_{R,0}$, and according to (2), the maximum extent of reaction becomes

$$\xi_{\max} = \min_R \left(\frac{n_{R,0}}{|\nu_R|} \right) \quad (4)$$

since the stoichiometric number of the reactants is negative, $|\nu_R| = -\nu_R$. Thus the maximum extent of reaction is defined as the minimum value of the quotient $n_{R,0}/|\nu_R|$ in the set for all reactants. The limiting reactant is hence the particular one from the set of all reactants for which this quotient has the minimum value.

Equation (3) implies that the initial extent of reaction is equal to zero, $\xi_0 = 0$, which is the most commonly used value for the state when the chemical amount of at least one of the reaction products is zero. The amounts of reactants and products are according to (2) given by

$$n_B = n_{B,0} + \nu_B \xi \quad (5)$$

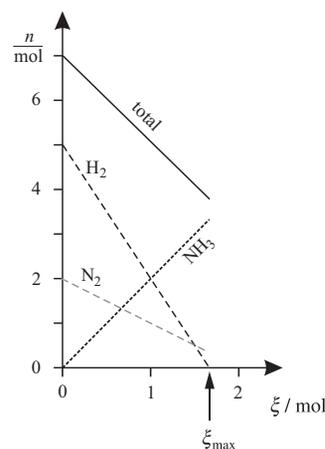


Figure 1. Variation of the amounts of individual substances in the synthesis of ammonia, $3 \text{H}_2 + \text{N}_2 \rightleftharpoons 2 \text{NH}_3$, as well as the total amount with the extent of reaction.

The amounts of species taking part in the reaction vary linearly with the extent of reaction and the slope of the lines define the stoichiometric coefficients. An example for the formation of ammonia ($3 \text{H}_2 + \text{N}_2 \rightleftharpoons 2 \text{NH}_3$) for given initial amounts ($n_0(\text{H}_2) = 5 \text{ mol}$; $n_0(\text{N}_2) = 2 \text{ mol}$; $n_0(\text{NH}_3) = 0$) is shown in Figure 1.

It is important to note that the extent of reaction, *i.e.* the chemical amount of transformations, is an extensive property. There are more reaction events taking place in a large system than in a small one. Many authors prefer to describe the progress of a reaction in terms of the degree of reaction (3), an intensive quantity describing the fraction a reaction has progressed from the initial state ($\xi_0 = 0$, $\alpha = 0$) toward completion ($\xi = \xi_{\max}$, $\alpha = 1$). The rather confusing terminology and notation has been described by Dumon *et al.*⁷

The stoichiometric number or stoichiometric coefficient is usually described as the number appearing in the reaction equation and emphasizing that it is negative for the reactants and positive for the products. A derived quantity should be defined in terms of previously defined quantities and I would prefer equation (2) to be regarded as the definition of the stoichiometric number. The amount of entities B is a base quantity and the extent can be defined by Eq. (1). Consequently Eq. (2) is a consistent and valid definition. For some time I thought that Kallay and I were the first to propose such a definition of the stoichiometric number,^{8,9} but recently by reading H. Bent's book *The Second Law*¹⁰ I found that already in 1965 he wrote that the stoichiometric number might be written as

$$\nu_B = \frac{dn_B}{d\xi} \quad (6)$$

which represents the slope of the lines in Figure 1.

Some chemists raise another objection to definition (1) in that the reaction events denoted by the chemical reaction equation are only rarely those actually taking

place. They are usually not elementary processes, but rather only some average resulting reaction from a series of elementary steps comprising a mechanism. Stoichiometric equations are helpful for accounting purposes only as required in stoichiometric calculations. This is much the same as using symbols of the elements and their standard atomic weights. For instance, we know that only in exceptional cases will the standard atomic weight correspond to the actual value for an individual atom. Thus there is no chlorine atom of relative mass 35.453, although the standard atomic weight is quoted as such and in most stoichiometric calculations this value is used. Similarly H^+ does not denote a proton, although often termed this way when considering acid dissociation, but a hypothetical average particle (so-called hydron) in an isotopic mixture of protons, $^1H^+$, and deuterons, $^2H^+$.

As a result, we have a somewhat illogical situation that many chemistry textbooks deal with energy changes associated with chemical reactions and with rates of chemical processes without ever describing properly how the advancement of such processes is expressed. Many chemists still hesitate to say what units are used to express the advancement of a chemical reaction: grams, moles, percents, seconds or any other. The corresponding enthalpy changes are sometimes expressed in kilojoules, sometimes in kilojoules per mole, or kilojoules per gram. The mole and gram are then often referred to a particular reactant or product, rather than to the process itself. The rates of reactions are also often ambiguously described. While there is never a problem in discussing radioactivity in terms of numbers of decays within a time interval, there are definitely a lot of difficulties involved in describing chemical reaction rates in terms of numbers or amounts of reaction events within a given time interval.⁹ It is important that the progress of a reaction is described in terms of the extent of reaction in order to enable one to define reaction enthalpies, internal energies, entropies or rates of reactions.

THE GIBBS FUNCTION

The Gibbs function or Gibbs energy formerly called free energy or sometimes after the German usage free enthalpy, is a thermodynamic function based on the enthalpy and entropy of the system and is of great importance for chemists investigating reactions at constant temperature and pressure as is usually the case. It provides the main basis for the criterion of spontaneity of chemical processes and chemical equilibrium. The concept is mentioned in most high school curricula, it is described in all General Chemistry textbooks, it is treated in detail in Physical Chemistry texts and, of course, in advanced thermodynamic literature. Many articles have been published throughout the past 50 years or so in journals on chemistry education attempting to familiarize teachers

and students with this complex concept. The complexity is obviously also reflected in the variety of names used for this function. The present article is yet another attempt to shed some light on the variation of the Gibbs function during a reaction.

Let me just repeat briefly the main definitions which are well described in easily available textbook literature. The definition of the Gibbs function is

$$G \stackrel{\text{def}}{=} H - TS$$

where H denotes the enthalpy, S the entropy and T the thermodynamic temperature. The change of Gibbs function at constant temperature is

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

It can be shown that this change is nothing but the change in total entropy, *i.e.* the entropy of the system and its surroundings, multiplied by the negative temperature¹¹

$$\Delta G = -T (\Delta S)_{\text{tot}} \quad (7)$$

According to the Second law of thermodynamics the total entropy increases in spontaneous processes, so that as an immediate consequence the Gibbs function of the system decreases. Its minimum defines the state of equilibrium. The total energy is constant and it is only the total entropy that has a tendency to change¹² (increase) in spontaneous processes. In line with Eq. (7) the Gibbs function will have a tendency to decrease. It is for this reason that I try to avoid the name energy and prefer Gibbs function to Gibbs energy or free energy.

Another important property of the Gibbs function is that its natural variables,⁶ pressure and temperature, are both intensive, which can easily be kept constant while the composition of the system changes in a chemical reaction. This is the reason why this function is of utmost importance in investigations of chemical equilibria. For a reaction mixture an infinitesimal change of the Gibbs function can be written as

$$dG = V dp - S dT + \sum \mu_J dn_J \quad (8)$$

where μ_J denotes the chemical potential or partial molar Gibbs function of species J taking part in the reaction

$$\mu_J = \left(\frac{\partial G}{\partial n_J} \right)_{p, T, n'}$$

Here n' denotes the set of amounts of all species in the system except for J. Equation (8) is often termed the fundamental equation of chemical thermodynamics.⁶

At constant pressure and temperature Eq. (8) reduces to

$$dG = \sum \mu_J dn_J \quad (9)$$

and the Gibbs function itself can be written as

$$G - G_0 = \sum \mu_J n_J \quad (10)$$

where G_0 is an arbitrarily chosen value with respect to which the Gibbs function is measured. During a chemical reaction at constant temperature and pressure the chemical amounts of individual species J change. So do the chemical potentials, even for ideal systems, because the spontaneous mixing process by itself contributes to the Gibbs function.

Let us first consider two well known examples: (i) the ice-water equilibrium and (ii) nitrogen dioxide dimerization.

The ice-water equilibrium is a type of phase equilibrium which is established when the molar Gibbs functions of the two phases are equal. At higher temperatures the Gibbs function of ice is higher than that of water and the spontaneous change from higher to lower Gibbs function is associated with the melting of ice. At lower temperatures the opposite process occurs since the Gibbs function of ice is lower than that of water. The two processes will both proceed to completion, that is, to the state of lowest value of the Gibbs function.

Nitrogen dioxide dimerization, from the brown gas NO_2 to its gaseous colourless dimer N_2O_4 , is an often considered and well known reaction to chemists. Every chemist is familiar with the fact that by heating the mixture by some 50 K above room temperature the colour will change to dark brown due to the dominance of the coloured NO_2 species. By cooling the mixture to *ca.* -10°C , it will become almost wholly transparent due to the dominance of the colourless N_2O_4 species. But even at such large temperature differences we would expect both species to be present in both the hot and the cold mixture. In the cold mixture a yellowish hue indicates the presence of NO_2 even by the naked eye.

Physical processes such as melting or freezing, evaporation or condensation go to completion as soon as the temperature is changed from the transition temperature value. Ice and water are at equilibrium when the temperature is 0°C (at normal pressure), but by changing the temperature to 1°C all the ice will melt, or by lowering the temperature to -1°C all the water will freeze. What is there so fundamentally different from a chemical equilibrium at a given temperature? This difference has nothing to do with a process usually being called physical and the other being called chemical. As pointed out by Trep-tow¹³ it has to do with one being heterogeneous and the other homogeneous, heterogeneity implying that the solubilities of non-liquid phases are negligible. It is this particular effect of mixing of reactants and products which I would like to address here, since I feel that it has been largely neglected or, at least, too rarely emphasized in texts describing chemical equilibria.

PERFECT GAS REACTIONS

In the following discussion of the variation of the Gibbs function with the advancement of the chemical process we shall restrict ourselves to perfect gases. The chemical potential of any perfect gas J is given by

$$\mu_J = \mu_J^\circ + RT \ln(p_J / p^\circ) \quad (11)$$

where μ_J° is the standard chemical potential of J , *i.e.* the chemical potential of pure gas J at standard pressure, p° , exhibiting ideal behaviour. The standard pressure, p° , is usually chosen to be the IUPAC recommended value¹⁴ of 10^5 Pa. Prior to 1982 it was usually the slightly higher normal atmospheric pressure of a standard atmosphere ($1 \text{ atm} = 101\,325 \text{ Pa}$). By writing the partial pressure of gas J as $p_J = y_J p$ where y_J is the amount fraction (mole fraction) and p the total pressure of the gas, Eq. (11) can be rewritten as

$$\mu_J = \mu_J^\circ + RT \ln(y_J p / p^\circ)$$

$$\text{or} \quad \mu_J = \mu_J^\circ + RT \ln(p / p^\circ) + RT \ln(y_J) \quad (12)$$

For real gases the partial pressure would have to be replaced by the fugacity, f_J , but the simple relationship would still remain

$$\mu_J = \mu_J^\circ + RT \ln(f_J / p^\circ)$$

By inserting (12) into (10) we obtain for the Gibbs function

$$G - G_0 =$$

$$\sum n_J \mu_J^\circ + nRT \ln(p / p^\circ) + \sum n_J RT \ln y_J \quad (13)$$

where n is the sum of amounts of all species $n = \sum n_J$.

The first term on the right-hand side represents the standard Gibbs energy of all the species in the system, implying that they are pure (unmixed) and at standard pressure. This term depends linearly on the extent of reaction since the amount of each substance taking part in the reaction depends linearly on ξ (see Eq. (5)) and we shall denote it $G^*(p^\circ)$. The asterisk * reminds us that the substances are pure.

The second term represents the correction when the constant total pressure differs from the standard pressure p° and vanishes when the total pressure is equal to the standard pressure. It depends on the total amount of species in the system and is also linearly dependent on the extent of reaction as shown in Figure 1. We shall denote the sum of the first two terms by $G^*(p)$.

The third term on the right-hand side of Eq. (13) represents the Gibbs function of mixing, $(\Delta G)_{\text{mix}}$. This term is negative since fractions are always less than one and the corresponding logarithms are negative. Mixing is a

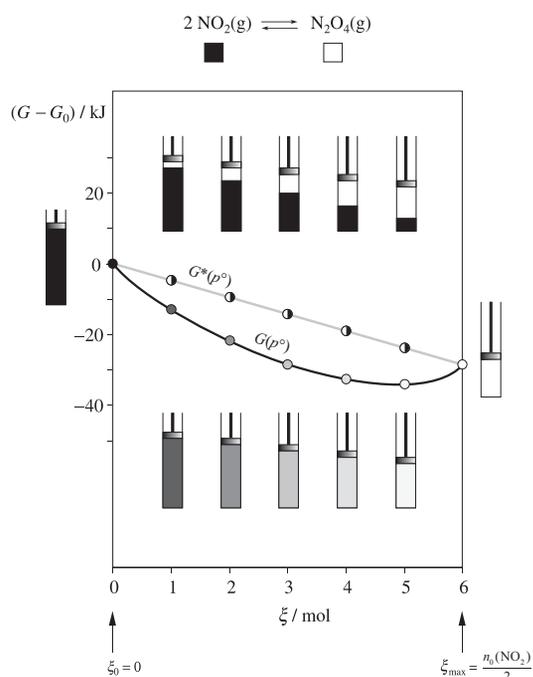


Figure 2. Variation of the Gibbs function with the extent of reaction given above and given initial amounts $n_0(\text{NO}_2) = 12$ mol and $n_0(\text{N}_2\text{O}_4) = 0$.

spontaneous process connected with a reduction of G . This term is the only one that does not have a linear dependence on the extent of reaction and is the one responsible for the Gibbs function to have a minimum between $\xi = 0$ and $\xi = \xi_{\text{max}}$.

A simple example of a gaseous equilibrium is the dimerization of nitrogen dioxide as already mentioned. Let us take the initial amount of NO_2 to be 12 moles, the maximum extent of the reaction $2 \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ is then 6 moles. The standard Gibbs functions of formation at 25 °C are taken from tabulated data¹⁵ as 51.31 kJ mol⁻¹ for $\text{NO}_2(\text{g})$ and 139.46 kJ mol⁻¹ for $\text{N}_2\text{O}_4(\text{g})$. The variation of the Gibbs function with the extent of reaction at standard pressure as calculated from (13) is given in Figure 2. The straight line represents the variation of $G^*(p^\circ)$, *i.e.* how the Gibbs function would change if there were no mixing of the gases involved. Schematically this is represented by the cylinders above. The real process involves also the mixing so that the resulting variation is given by the curve and schematically represented by the paler mixtures in the cylinders below. The real process at standard pressure can be split into two steps: (i) the change in G due to the changes in amounts of the unmixed reacting species (step $T_0 \rightarrow T_1$ in Figure 3) and (ii) the mixing of the gases at constant extent of reaction (step $T_1 \rightarrow T_2$ in Figure 3). The first step is represented by the first term in Eq. (13), and the second step by the third term. The second term vanishes at standard pressure.

^(a) relative with respect to the standard pressure

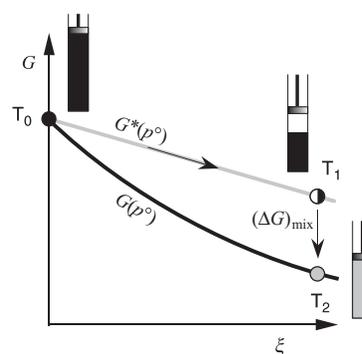


Figure 3. The change of the Gibbs function with the extent of reaction from T_0 to T_2 can be split into two hypothetical steps: one involving unmixed substances and the other their mixing.

The affinity of the reaction, *i.e.* its tendency to advance, is given by the slope of the Gibbs function with respect to ξ . This slope varies from a highly negative value at ξ_0 to zero at equilibrium when the Gibbs function has a minimum value and further on to a highly positive value at ξ_{max} , as seen for the curve $G(p^\circ)$ in Figure 2. The slope of G can be derived from (9) by inserting $v_j d\xi$ for dn_j giving finally

$$\left(\frac{\partial G}{\partial \xi} \right)_{p,T} = \sum v_J \mu_J \quad (14)$$

By substituting (12) for μ_J and introducing the common somewhat shorter notation we obtain for the slope of the Gibbs function the so-called Gibbs function of the reaction

$$\Delta_r G = \sum v_J \mu_J^\circ + vRT \ln(p/p^\circ) + \sum v_J RT \ln y_J$$

$$\text{or } \Delta_r G = \Delta_r G^\circ + vRT \ln(p/p^\circ) + RT \ln \left(\prod_J y_J^{v_J} \right) \quad (15)$$

$$\text{or } \Delta_r G = \Delta_r G^\circ + RT \ln \left(\prod_J (y_J p/p^\circ)^{v_J} \right) \quad (16)$$

We see from (15) that there are three contributions to the slope $\Delta_r G = (\partial G/\partial \xi)_{p,T}$. The first term on the right-hand side represents the standard Gibbs function of the reaction $\Delta_r G^\circ = \sum v_J \mu_J^\circ$. It is the slope of the line $G^*(p^\circ)$ in Figure 2. The second term vanishes for standard pressure, $p = p^\circ$, or when the sum of stoichiometric coefficients is equal to zero $v = \sum v_J = 0$. Both contributions are independent of ξ (straight lines have constant slopes). The third term represents the contribution of mixing to the slope. It varies strongly with changing composition. The product in the logarithmic argument is often termed the reaction quotient in terms of amount fractions (mole fractions) in Eq. (15) or in terms of relative^(a) partial pressures,

$p_j/p^\circ = y_j p/p^\circ$, in (16). The product becomes a quotient when the reactants and products are grouped separately

$$Q = \prod_J (p_J / p^\circ)^{\nu_j} = \frac{\prod_P (p_P / p^\circ)^{\nu_P}}{\prod_R (p_R / p^\circ)^{|\nu_R|}} \quad (17)$$

The stoichiometric numbers for the reactants are negative and can be written as $\nu_R = -|\nu_R|$. In order to have positive values in the exponents the factors for the reactants are usually written in the denominator yielding the more familiar expression on the right and justifying the name reaction quotient.

The equilibrium is defined by the minimum of the Gibbs function when the slope (16) is equal to zero. It follows immediately that

$$\Delta_r G^\circ = -RT \ln \left(\prod_J (y_{J,e} p / p^\circ)^{\nu_j} \right) = -RT \ln K^{\text{id}}$$

The product of partial pressures at equilibrium divided by the standard pressure is the equilibrium constant for ideal gases K^{id} . For real gases the analogous expression would be

$$\Delta_r G^\circ = -RT \ln K^\circ \quad (18)$$

where K° is the so-called standard or thermodynamic equilibrium constant. This indeed is the thermodynamic definition of the equilibrium constant.¹ There is a subtle difference in what meaning chemists attach to the symbol $^\circ$ for a standard function X° . For some including myself, following Guggenheim, the symbol denotes merely that the value depends on a convention (what is the standard pressure, molality or concentration) and that X° is a function of temperature only. Others, following American usage, regard X° to be the value of X in the, usually hypothetical, standard state. In their opinion the symbol K° and the name standard equilibrium constant are simply wrong for K reflects the equilibrium composition and not the pure perfect gas behaviour at standard pressure.

One more property of diagrams such as given in Figure 2 has to be mentioned. The extent of reaction on the abscissa is an extensive quantity. It depends on a particular chosen system and in our case it extends from zero to 6 moles. The corresponding values of ΔG on the ordinate are also dependent on the particular system: the changes would be smaller for a smaller system. The minimum of the function would be at a smaller value of ξ . Some authors prefer therefore to plot the dimensionless degree of reaction on the horizontal axis, while others choose a system for which the extent of reaction varies from 0 to 1 mole. In the former case the slopes of the lines have the same dimension as the ordinate: they are extensive properties referring to a particular system. In the latter case only a different particular system is chosen as

if we had divided the values on both axes by six. The slope of G with respect to ξ describing the spontaneity of the process is related to the slope of G vs. α according to (3)

$$\left(\frac{\partial G}{\partial \xi} \right)_{p,T} = \left(\frac{\partial G}{\xi_{\text{max}} \partial \alpha} \right)_{p,T}$$

which can be written as

$$\left(\frac{\partial G}{\partial \xi} \right)_{p,T} = \left(\frac{\partial(G/\xi_{\text{max}})}{\partial \alpha} \right)_{p,T} \quad (19)$$

In the right-hand-side expression the quantities G/ξ_{max} and α are both intensive and diagrams of the type given in Figure 2 will be independent of the size of the system but just on the substances involved, the ratio of initial amounts, temperature and pressure. This will be shown in the next example.

A GENERAL CASE

Let us examine a general reaction



The chemical potentials of the substances are set to be 10, 16, 20 and 12 kJ/mol for A, B, C, and D, respectively, and the initial amounts are set at $n_{\text{A},0} = 4$ mol, $n_{\text{B},0} = 2$ mol, $n_{\text{C},0} = n_{\text{D},0} = 0$. The dependence of the first term in Eq. (13) on the extent of reaction is represented by the line $G^*(p^\circ)$ between points M and N in Figure 4. Point M represents the initial state when the two reactants are not mixed and at standard pressure (schematically represented by the cylinder on the left). Similarly point N represents the state of the two unmixed products C and D. The slope of the line according to (19) gives the standard Gibbs function of the reaction and is related *via* (18) to the standard equilibrium constant.

If the pressure is increased to 5 times the standard value, $5p^\circ$, the Gibbs function will increase as given by the second term in Eq. (13). This increase is greater for the reactants (from point M to P) than for the products (from N to Q) at $\alpha = 1$ because the total amounts of substances are greater at the beginning than at the end. This is why the slope of the line $G^*(5p^\circ)$ from P to Q is steeper than at lower pressure $G^*(p^\circ)$. By taking into account the mixing process, that is the third term in Eq. (13), the curve $G(5p^\circ)$ is obtained. The contribution of mixing of A and B at the initial stage is represented by a decrease of the Gibbs function divided by the maximum extent of reaction from point P to R and illustrated by the cylinders on the left. Similarly the effect of mixing of the products is represented by a shift from Q to S and illustrated by the cylinders on the right. The curve $G(5p^\circ)$ has a minimum corresponding to the equilibrium position at the degree $\alpha = 0.76$.

When the total pressure is reduced to half of the standard value, $0.5 p^\circ$, the line $G^*(0.5p^\circ)$ and curve $G(0.5p^\circ)$ are obtained. The slope of the line representing the reaction when the substances are separated is now less negative than at standard pressure $G^*(p^\circ)$ and by adding the effect of mixing (third term in Eq. (13)) the resulting curve has a minimum at a lower value of the degree of reaction. The shift of the minimum from $\alpha_e(5p^\circ)$ to $\alpha_e(0.5p^\circ)$ represents the shift of the equilibrium of the studied system when the total pressure is reduced tenfold from $5 p^\circ$, as expected from the Le Chatelier principle. The corresponding changes of amounts of reactants or products are obtained by multiplying the degrees of reaction by the maximum extent of reaction and stoichiometric numbers. The changes of Gibbs function can be calculated in the same simple way. Thus, the diagrams shown in Figure 4 do not depend on the initial amounts of reactants *i.e.* on the size of the system, just on their ratio. The diagram will remain the same whether we take the initial conditions as given above or by multiplying the initial amounts by any given factor. The slopes of the lines and

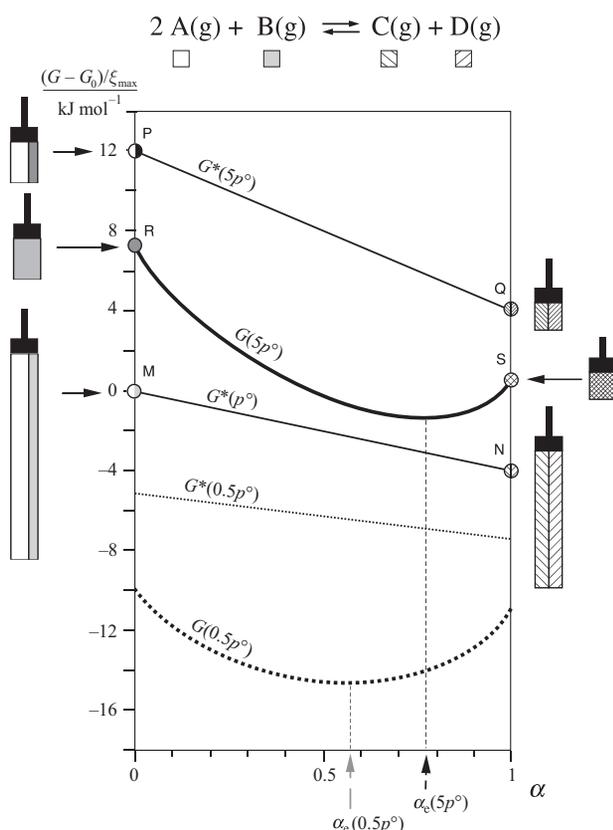


Figure 4. Variation of the Gibbs function with the degree of reaction split into three contributions. The line $G^*(p^\circ)$ shows the variation of the standard Gibbs function the other two straight lines include the corrections for different pressures and the two curves include the effect of mixing and represent the variation of the total Gibbs function. The two axes represent intensive quantities and the diagram is hence independent of the size of the system.

curves in these diagrams do not depend on the size of the system. They are according to (19) the same as given for a plot of G vs. ξ as shown in Figure 2.

The meaning of the slope of the line $G^*(p^\circ)$ is well documented as $\Delta_r G^\circ = \sum \nu_j \mu_j^\circ$ in the literature. In line with what was said about the meaning of the standard functions this slope depends on temperature only. However, the slopes of the lines $G^*(p)$ at other pressures which take into account the pressure correction (second term in Eq. (15)) are different when the sum of stoichiometric numbers is not zero. The slopes are given by the sum of the first two terms on the right-hand side of Eq. (15)

$$\frac{\partial G^*(p)}{\partial \xi} = \frac{\partial(G^*(p)/\xi_{\max})}{\partial \alpha} = \Delta_r G^\circ + \nu RT \ln(p/p^\circ) \quad (20)$$

The slope at the minimum of the curves denoted $G(p)$, the total pressure being $p = 5 p^\circ$ and $p = 0.5 p^\circ$ in Figure 4, is equal to zero. The product in the logarithmic argument is then equal to the equilibrium constant in terms of amount fractions

$$K_y(p) = \prod_j y_{j,e}^{\nu_j} \quad (21)$$

and we can conclude from (15) that the slopes of the lines $G^*(p)$ (20) are equal to

$$\frac{\partial G^*(p)}{\partial \xi} = -RT \ln(K_y(p))$$

where the equilibrium constant K_y is clearly dependent on total pressure.

A spread sheet program (MS Excel) has been devised in order to show visually how the pressure, temperature or ratio of initial amounts affects the variation of the Gibbs function and the equilibrium composition. The reaction type is the same as described here, but it can be changed by setting some stoichiometric coefficients to zero. Additional input data required are the Gibbs functions of formation and enthalpies of formation for all the substances involved at 298 K, total pressure and temperature. The program with more detailed description can be obtained from the author upon request or downloaded from the following address: <ftp://ftp.chem.pmf.hr/download/cvitas/ccal/>.

CONCLUSION

It is proposed here to define the extent of reaction simply as the chemical amount of reactions (moles of reactions) and consequently define the stoichiometric number by Eq. (6) as H. Bent did already in 1965. The variation of Gibbs function in an ideal gas system undergoing a chemical change at constant temperature and pressure with the extent of reaction is described in detail. It was shown that the most convenient way to present the behaviour of the Gibbs function is to plot $\Delta G/\xi_{\max}$ as a function of the degree of reaction.

Acknowledgement. – The financial support by the Ministry of Science, Education and Sports of the Republic of Croatia is gratefully acknowledged.

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SAŽETAK

Gibbsova funkcija kemijske reakcije

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Definiranjem dosega reakcije kao množine kemijskih pretvorbi iskazanih jednadžbom reakcije stehiometrijski se broj neke jedinice koja sudjeluje u reakciji može definirati promjenom množine tih jedinica s promjenom dosega. Promjena Gibbsove funkcije pri napredovanju reakcije analizirana je u detalje za sustav reagirajućih idealnih plinova pri stalnoj temperaturi i tlaku. Same promjene rastavljene su u tri doprinosa: standardna Gibbsovu funkciju reakcije, korekcija u slučaju odstupanja tlaka od standardne vrijednosti i doprinos miješanja. Prva dva doprinosa linearno ovise o dosegu reakcije, a treći je jedini koji uzrokuje postojanje minimuma Gibbsove funkcije pa tako i ravnoteže između minimalnog i maksimalnog dosega, odnosno pri stupnju reakcije između 0 i 1. Kao najpovoljniji prikaz dana je ovisnost promjene Gibbsove funkcije podijeljene s maksimalnim dosegom reakcije o stupnju reakcije. Takav prikaz ne ovisi o veličini sustava nego samo o prirodi reakcije, temperaturi, tlaku i omjeru početnih množina reagirajućih tvari. U posebnom dodatku dan je Excel-program koji za dane podatke prikazuje odgovarajuće ovisnosti Gibbsove funkcije o stupnju reakcije.