
CALCULATION OF A COMPLEX CHEMICAL EQUILIBRIUM IN REAL GASEOUS SYSTEMS USING THE GENERALIZED REDLICH-KWONG EQUATION

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A general and never failing to converge method was suggested for calculating the equilibrium composition of real gaseous system whose components react chemically. To express the pressure-volume-temperature behaviour the Redlich-Kwong equation in generalized form was used. The application of the method is illustrated on three industrially important examples.

For calculating complex chemical equilibria in an ideal gaseous state, a number of method is available at present based on the knowledge of equilibrium constants of single reactions as well as on the minimization of the total free enthalpy of system (see for instance^{1,2}). Considering that most organic reactions in the gas phase take place at the temperatures at which, as a rule, all components are in the supercritical region, the presumption of ideal behaviour is rather well fulfilled under normal or moderate pressures. However, a number of industrially employed reactions is known as well which begin to be of interest only under pressures at which single components and their mixtures already exhibit a considerable deviations from ideal behaviour. It is so *e.g.* in synthesis of ammonia, methanol, hydroformylation of olefins, synthesis of amines from olefins and ammonia, oxidative cleavage of hydrocarbons and many others. In such cases it is not possible to neglect the effect of non-ideal behaviour. As far as the processes are concerned whose course is expressed by the only reaction the pressure-volume-temperature behaviour of single components and the mixture is either known or it can be estimated³ with a relatively good accuracy. The determination of equilibrium composition for a nonideal mixture does not make then any difficulties. However, if the reacting system is more complex the pressure-volume-temperature relations are not known as a rule nor is it possible to assume that they could be measured. Considering that it is difficult to estimate how great effect the real behaviour of mixture on equilibrium composition will have, it seems advantageous to have at our disposal a method in which this effect could be expressed. Such a method should be both sufficiently accurate and as far as possible general and it should not cause moreover an excessive complication of mathematic relations. It is evident that these requirements are satisfied best by such

procedures which are based on the knowledge of pressure–volume–temperature relations of pure components.

In the present work the method is described. To determine the equilibrium composition the way of determining the minimum of total free enthalpy in terms of the Lagrange multipliers, and to describe the nonideal behaviour of mixture the generalized Redlich–Kwong equation are chosen.

Formulation of the Problem

The determination of chemical equilibrium in a closed system at constant temperature and pressure is equivalent to the finding of minimum of the Gibbs function

$$G = \sum_{i=1}^N n_i \mu_i \quad (1)$$

on the set of points (n_1, n_2, \dots, n_N) satisfying the conditions

$$\sum_{i=1}^N a_{ij} n_i = b_j, \quad j = 1, 2, \dots, M. \quad (2)$$

In Eqs (1) and (2) N denotes number of components, M number of elements, n_i number of moles of the i -th component, μ_i chemical potential of the i -th component in mixture, a_{ij} constitutional coefficient (number of gram-atoms of the j -th element in the i -th component) and b_j total number of gram-atoms of the j -th element in system. The system of equations (2) expresses a mass balance of system. For the chemical potential μ_i holds

$$\mu_i = \mu_i^0 + RT \ln f_i = \mu_i^0 + RT(\ln x_i P + \ln \varphi_i), \quad (3)$$

where μ_i^0 is chemical potential of pure component at a temperature of system, at a pressure of 1 atm and in an ideal gaseous state, f_i is fugacity of the i -th component in mixture, φ_i fugacity coefficient of the i -th component in mixture, P total pressure, x_i mole fraction ($x_i = n_i/n$, where $n = \sum_{i=1}^N n_i$), T is temperature in Kelvin degrees, and R gas constant. On substituting Eq. (3) into Eq. (1) we get

$$Q = \sum_{i=1}^N n_i (c_i + \ln \varphi_i + \ln n_i/n), \quad (4)$$

where

$$c_i = \mu_i^0/RT + \ln P, \quad Q = G/RT. \quad (5), (6)$$

For an ideal mixture of ideal gases is $\varphi_i \equiv 1$, for an ideal mixture of real gases ($f_i = x_i f_i^0$, where f_i^0 is fugacity of pure component at a temperature and pressure of system) is $\varphi_i = \varphi_i^0$, where φ_i^0 is fugacity coefficient of pure component at a temperature and pressure of system. Only for the real mixture of real gases φ_i is also a function of mixture composition.

Numerical Solution

Let us assume first that we solve the problem of an ideal mixture of ideal or real gases. Let us denote

$$p_i = c_i + \ln \varphi_i, \quad i = 1, 2, \dots, N, \quad (7)$$

where p_i is a quantity independent of the mixture composition. The finding of the point of minimum of a function

$$K(n_1, n_2, \dots, n_N, \lambda_1, \dots, \lambda_M) = Q(n_1, n_2, \dots, n_N) + \sum_{j=1}^M \lambda_j (b_j - \sum_{i=1}^N a_{ij} n_i) \quad (8)$$

is equivalent to the solution of the problems (4) and (2). The quantities λ_j are the Lagrange multipliers. By differentiating the function K with respect to n_i we obtain

$$x_i = \exp \left(\sum_{k=1}^M a_{ik} \lambda_k - p_i \right), \quad i = 1, 2, \dots, N. \quad (9)$$

A more detailed procedure is given in one of foregoing papers⁴. The system (2) can be rewritten into the form

$$\sum_{i=1}^N a_{ij} x_i - b_j t = 0, \quad j = 1, 2, \dots, M, \quad (10)$$

$$\sum_{i=1}^N x_i = 1, \quad t = 1/n.$$

On eliminating the unknown t from the first equation (10) we obtain the system

$$\sum_{i=1}^N a_{ij} x_i = d_j, \quad j = 1, 2, \dots, M, \quad (11)$$

where

$$q_{i1} = 1; \quad d_1 = 1; \quad d_j = 0, \quad j = 2, \dots, M, \quad (12)$$

$$q_{ij} = a_{ij} - a_{i1} b_j / b_1, \quad j = 2, \dots, M.$$

When substituting Eq. (9) into Eq. (11) we get the system of M equations for M unknown quantities $\lambda_1, \lambda_2, \dots, \lambda_M$ in the form

$$\sum_{i=1}^M q_{ij} \exp \left(\sum_{k=1}^M a_{ik} \lambda_k - p_i \right) = d_j, \quad j = 1, \dots, M. \quad (13)$$

A numerical solution of the system of equations (13) is not easy. On using the Newton method we meet with difficulty when estimating the first approximation $\lambda_j^{(0)}$. With respect to relatively large values of $|p_i|$ it is difficult to find $\lambda_j^{(0)}$ so that the values $x_i^{(0)}$ calculated from the relation (9) should lie in the interval (0.1) and lest most values $x_i^{(0)}$ should be nearly zero. Such a case must be prevented because as a result badly conditioned matrices are obtained resulting in a very unstable numerical process. The substance of difficulties during the numerical solution of the system (13) consists in the fact that in the exponent on the right-hand side of the relation (9) there is a difference of two large numbers. The use of non-derivative methods fails as well for it is possible to show that the function

$$W(\lambda_1, \lambda_2, \dots, \lambda_M) = \sum_{j=1}^M (d_j - \sum_{i=1}^N q_{ij} \exp \left(\sum_{k=1}^M a_{ik} \lambda_k - p_i \right))^2 \quad (14)$$

has more points in which it acquires its relative minimum. Our aim is therefore the choice of such a numerical method to be able to use the value $x_i^{(0)}$ as the first approximation instead of $\lambda_j^{(0)}$. This can be reached in the following way: If we take logarithm of the left- and right-hand side of Eq. (9) and expand the left-hand side of the equation obtained in this way in the Taylor series with two first terms we get

$$x_i^{(1)} = x_i^{(0)} + \Delta x_i, \quad (15)$$

where

$$\Delta x_i = x_i^{(0)} \left(-\ln x_i^{(0)} + \sum_{k=1}^M a_{ik} \lambda_k - p_i \right). \quad (16)$$

By substituting Eqs (15) and (16) into Eq. (11) and by solving the resulting linear system, we obtain the values $\lambda_k, k = 1, 2, \dots, M$. From the obtained values λ_k we can determine $x_i^{(1)}, i = 1, 2, \dots, N$. We use for it a reducing parameter $\varepsilon \in (0.1)$, *i.e.*

$$x_i^{(1)} = x_i^{(0)} + \varepsilon \cdot \Delta x_i, \quad (17)$$

which is chosen so that $x_i^{(1)} \in (0.1)$ for all $i = 1, 2, \dots, N$. Considering that $x_i^{(0)} \in (0.1)$ then such $\varepsilon > 0$ is evident to exist. The above-said numerical procedure is repeated till holds

$$\sum_{k=1}^M a_{ik} \lambda_k - p_i < 0, \quad i = 1, 2, \dots, N, \quad (18)$$

i.e. the values of x_i calculated from the relation (9) are smaller than one. The first stage of calculation ends here. The values λ_j obtained in this way are used as the first approximation in the Newton method by means of which the system of equations (13) is solved. In the second stage of calculating we also use the reducing parameter $\varepsilon \in (0; 1)$ so that

$$\lambda_k^{(1)} = \lambda_k^{(0)} + \varepsilon \Delta \lambda_k. \quad (19)$$

The value of ε is chosen so that the nonequalities (18) could hold even for a new approximation of values λ_k .

Let us come back to the problems of choosing the first approximation of $x_i^{(0)}$. We can proceed in several ways (only those which have been verified in practice are given):

1) We now approximate values of equilibrium composition. This case can occur *e.g.* if we calculate equilibrium composition of the same mixture at the same temperature but at another pressure.

2) We choose $x_i^{(0)} = 1/N$. In this case we do not use any information on the system.

3) From Eq. (2) it is evident that

$$n_i \leq q_i = \min_{j, a_{ij} \neq 0} (b_j / a_{ij}), \quad i = 1, 2, \dots, N.$$

Then we can choose $x_i^{(0)} = q_i / \sum_{r=1}^N q_r$. This approximation does not use thermodynamic properties of the given mixture (*e.g.* it is independent of temperature and pressure). It follows from relation (4) that the lower the value of p_i is the more hopeful the occurrence of the i -th component in equilibrium is. As far as all p_i are negative (the most often occurring case) then it is possible to choose

$$x_i^0 = q_i |p_i| / \sum_{r=1}^N q_r |p_r|, \quad i = 1, 2, \dots, N. \quad (20)$$

In our practice we have not found a case that the numerical process proposed would not converge even if the values $x_i^{(0)}$ are chosen according to any of three ways given.

Now there is a problem left of calculating the equilibrium composition of real mixture of real gases (φ_i is a function of composition). In this case we proceed so that the given system is solved as an ideal mixture of real gases first. The calculated composition is then used to determine p_i and the calculation is repeated. Usually additional two or three iteration cycles are sufficient.

Redlich-Kwong Equation and Reasons of Its Choice

To determine the fugacity coefficient φ_i the Redlich-Kwong equation in generalized form was chosen. This choice is to be supported by several reasons:

1) The accuracy of the equilibrium composition determination is conditioned by the accuracy of thermochemical quantities. It is evident from Eqs (4), (5), and (7) it is of no use to require higher accuracy in the determination of the logarithm of fugacity coefficient than the accuracy of the μ_i^0/RT determination from experimental data is. It follows from Eqs (7) and (9) that

$$\delta x_i/x_i \approx \delta(\mu_i^0/RT) + \delta(\ln \varphi_i), \quad i = 1, 2, \dots, N, \quad (21)$$

where δ is a symbol for absolute error. A considerable dependence of the accuracy in the equilibrium composition determination on the accuracy of the determination of values μ_i^0/RT can be seen from Eq. (21). If a maximum one-percent error in the equilibrium composition determination is to be warranted an absolute error smaller than 0.01 must be secured in the values of μ_i^0/RT and $\ln \varphi_i$. Such an accuracy is apparently worse reached in the relatively large value of μ_i^0/RT than in the value of $\ln \varphi_i$.

2) It is more reasonable to choose a simpler equation. A decrease in the accuracy of calculated fugacity coefficients is negligible. Besides, with the aim of the description of chemical equilibrium in a wide range of temperatures and pressures, the extrapolation outside the range of validity may be connected with a greater risk in case of multiconstant equations than with simple relations.

3) The Redlich-Kwong equation appears to be one of the best and most often used one among equations of state with low number of constants.

4) Its generalized form comply well with the intended aim to express nonideal behaviour from critical data which are easily available for a wide group of substances.

The generalized form of the equation can be written in the form

$$P = RT/(v - b) - a/[v(v + b) \sqrt{T}], \quad (22)$$

where $a = 0.4278(RT_c)^2 \sqrt{T_c}/P_c$, $b = 0.0867RT_c/P_c$. For the fugacity coefficient of pure component holds³

$$\begin{aligned} \ln \varphi_i^0 = & \ln [RT/(P(v - b_i))] + b_i/(v - b_i) - a_i[1/(v + b_i) + \\ & + b_i^{-1} \ln ((v + b_i)/v)]/(RT^{1.5}), \end{aligned} \quad (23)$$

where a_i , b_i are constants of the Redlich-Kwong equation for the i -th component and v is molar volume of the i -th component at the temperature and pressure of sys-

tem. If we use for calculating the fugacity coefficient of the component i in mixture the rules in the form

$$a = \left(\sum_{i=1}^N x_i \sqrt{a_i} \right)^2, \quad b = \sum_{i=1}^N x_i b_i, \quad (24)$$

then it can be shown that the relation holds³:

$$\ln \varphi_i = \ln \left(\frac{RT}{P(v-b)} + \frac{b_i}{v-b} - a \left\{ \frac{b_i}{b(v+b)} \right\} + \right. \\ \left. + \left[\frac{2\sqrt{a_i/a} - b_i/b}{b} \right] \cdot \ln \left(\frac{(v+b)/v}{RT^{1.5}} \right) \right). \quad (25)$$

where a, b are constants of mixture determined by Eqs (24) and v is molar volume of mixture at the temperature and pressure of system.

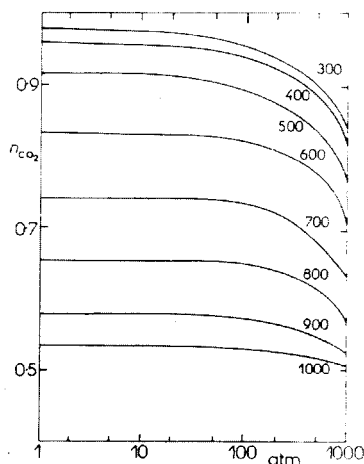


FIG. 1

Effect of Nonideal Behaviour (r-r Type) on Equilibrium Number of CO_2 mol at Various Temperatures

TABLE I
Dependence of Diethylamine Formation on Pressure

T, K	Type	P, atm									
		1	2	5	10	20	50	100	200	500	1000
600	i-i	0.1257	0.1861	0.2263	0.2391	0.2453	0.2489	0.2501	0.2507	0.2510	0.2511
600	i-r	0.1257	0.1863	0.2263	0.2389	0.2444	0.2445	0.2479	0.2560	0.2580	0.2528
600	r-r	0.1257	0.1863	0.2266	0.2397	0.2464	0.2514	0.2550	0.2584	0.2582	0.2540
700	i-i	0.0026	0.0097	0.0471	0.1115	0.1800	0.2323	0.2500	0.2586	0.2637	0.2653
700	i-r	0.0026	0.0098	0.0476	0.1128	0.1819	0.2335	0.2504	0.2615	0.2670	0.2644
700	r-r	0.0026	0.0098	0.0473	0.1121	0.1815	0.2352	0.2540	0.2637	0.2674	0.2649

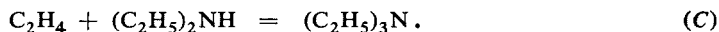
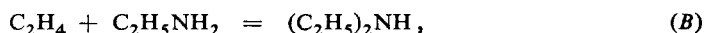
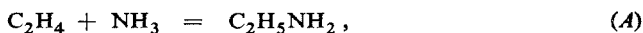
TABLE II
Equilibrium Composition of Ethane Thiol Synthesis at 80 atm

T, K	Type	Component, n_i									
		C_2H_5OH	H_2	S_2, g	C_2H_5SH	$(C_2H_5)_2S$	H_2S	$(C_2H_5)_2O$	CH_3CHO C_2H_6	C_2H_4	H_2O
400	i-i	$0.1782 \cdot 10^{-4}$	$0.3340 \cdot 10^{-8}$	$0.5876 \cdot 10^{-12}$	0.2060	0.2476	0.5465	$0.2976 \cdot 10^{-8}$	0.1494	$0.3471 \cdot 10^{-5}$	0.8505
400	i-r	$0.3901 \cdot 10^{-5}$	$0.1563 \cdot 10^{-8}$	$0.5933 \cdot 10^{-5}$	0.2634	0.3310	0.4055	$0.2160 \cdot 10^{-9}$	$0.3724 \cdot 10^{-1}$	$0.1572 \cdot 10^{-5}$	0.9627
400	r-r	$0.8520 \cdot 10^{-5}$	$0.1189 \cdot 10^{-9}$	$0.3430 \cdot 10^{-12}$	0.3070	0.3160	0.3770	$0.2657 \cdot 10^{-9}$	$0.3048 \cdot 10^{-1}$	$0.4651 \cdot 10^{-6}$	0.9695
500	i-i	$0.6374 \cdot 10^{-4}$	$0.4306 \cdot 10^{-6}$	$0.1419 \cdot 10^{-11}$	0.1854	0.7925	$0.7354 \cdot 10^{-1}$	$0.1613 \cdot 10^{-7}$	0.3279	$0.2786 \cdot 10^{-3}$	0.6720
500	i-r	$0.7233 \cdot 10^{-4}$	$0.4390 \cdot 10^{-6}$	$0.2296 \cdot 10^{-7}$	0.2075	0.1238	0.6687	$0.1346 \cdot 10^{-7}$	0.2724	$0.2073 \cdot 10^{-3}$	0.7275
500	r-r	$0.6572 \cdot 10^{-4}$	$0.2891 \cdot 10^{-6}$	$0.7029 \cdot 10^{-11}$	0.2126	0.9807	$0.6893 \cdot 10^{-1}$	$0.1440 \cdot 10^{-7}$	0.2955	$0.2251 \cdot 10^{-3}$	0.7045
600	i-i	$0.1130 \cdot 10^{-3}$	$0.1150 \cdot 10^{-4}$	$0.2265 \cdot 10^{-11}$	0.1256	0.2046	$0.8539 \cdot 10^{-1}$	$0.3025 \cdot 10^{-7}$	0.4147	$0.3927 \cdot 10^{-2}$	0.5851
600	i-r	$0.1190 \cdot 10^{-3}$	$0.1137 \cdot 10^{-4}$	$0.1831 \cdot 10^{-8}$	0.1396	0.2948	$0.8307 \cdot 10^{-1}$	$0.3046 \cdot 10^{-7}$	0.3990	$0.3623 \cdot 10^{-2}$	0.6009
600	r-r	$0.1162 \cdot 10^{-3}$	$0.9480 \cdot 10^{-5}$	$0.5122 \cdot 10^{-11}$	0.1388	0.2395	$0.8372 \cdot 10^{-1}$	$0.2955 \cdot 10^{-7}$	0.4047	$0.3694 \cdot 10^{-2}$	0.5952
700	i-i	$0.1246 \cdot 10^{-3}$	$0.1586 \cdot 10^{-3}$	$0.2950 \cdot 10^{-11}$	0.6665	$0.3468 \cdot 10^{-2}$	$0.9294 \cdot 10^{-2}$	$0.2835 \cdot 10^{-7}$	0.4480	$0.2939 \cdot 10^{-1}$	0.5518
700	i-r	$0.1628 \cdot 10^{-3}$	$0.1236 \cdot 10^{-3}$	$0.2943 \cdot 10^{-9}$	0.8901	0.7620	$0.9033 \cdot 10^{-2}$	$0.4559 \cdot 10^{-7}$	0.4369	$0.2202 \cdot 10^{-1}$	0.5630
700	r-r	$0.1600 \cdot 10^{-3}$	$0.1109 \cdot 10^{-3}$	$0.4724 \cdot 10^{-11}$	0.8782	0.6797	$0.9051 \cdot 10^{-2}$	$0.4424 \cdot 10^{-7}$	0.4382	$0.2214 \cdot 10^{-1}$	0.5616

The use of the method. Verification of the method was carried out by computing the equilibrium composition of some simple systems (thermochemical data were in all cases taken from the monograph of Stull and coworkers⁵).

1) Water-gas conversion: This simple reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) is very suitable to appreciate the effect of real behaviour because its course is not connected with a change in volume. The change of equilibrium composition with pressure is therefore solely a consequence of the effect of nonideal behaviour. The results of computation for the initial molar ratio $\text{CO} : \text{H}_2\text{O} = 1 : 1$ and the temperature range of 300–1000 K are represented in Fig. 1 as the number of moles of CO_2 formed, as a function of pressure.

2) Ammonia addition on ethylene: The reactions were considered resulting in ethyl-, diethyl-, and triethylamine formation:



For the ratio of initial components 1 : 1, the dependence of equilibrium number of moles of diethylamine formed at a temperature of 600 and 700 K on pressure is presented in Table I. Three cases are always considered, *viz.* an ideal mixture of ideal gases (denoted in the Table as i-i), an ideal mixture of real gases (i-r), and a real mixture of real gases (r-r).

3) The formation of ethanethiol and diethylsulphide from ethanol, hydrogen, and gaseous sulphur: Besides the starting components ethane thiol, diethyl sulphide, hydrogen sulphide, diethyl ether, acetaldehyde, ethylene, ethane, and water were considered in the reaction mixture. The results of computation for the equimolar composition of initial mixture ($\text{C}_2\text{H}_5\text{OH} : \text{H}_2 : \text{S}_2 (\text{g}) = 1 : 1 : 1/2$) under a pressure of 80 atm are presented in Table II as the number of moles of single components under corresponding temperatures as well for all three types of mixtures (i-i, i-r, r-r).

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