GENERAL PROBLEMS OF CHEMICAL THERMODYNAMICS

Modified Marcelin–de Donder Equations for the Kinetics of One- and Two-Step Reversible Chemical Reactions in Nonideal Solutions

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Abstract—An approach to a unified description of the kinetics of reversible chemical reactions on both sides of the equilibrium state was suggested. The description was based on the dynamic equilibrium principle, the isotherm–isobar equation for a chemical reaction, and the volume densities of the thermodynamic activities of the reagents (normalized by the pure component states). The equations obtained were applied to describe our own and literature data on the kinetics of acid-catalyzed transesterification reaction between butyl acetate and methanol at 298 K and esterification of ethylene glycol with acetic acid at 313 K. It was shown that the observed rate constant could be represented in the form of the sum of partial contributions describing the reactions in the presence of a large excess of one of the reagents.

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The problem of a theoretical description of the kinetics of reversible chemical reactions in nonideal solutions has been studied for about 100 years [1]. The traditional approach based on the law of mass action takes into account the influence of solvent properties through the equilibrium constants of formation of reactive reagent forms [2]. Most often, this allows the experimental data on a separate kinetic curve to be described fairly accurately.

A good description of separate kinetic curves unfortunately does not mean that the kinetics as a whole is described satisfactorily. In particular, rate constants change jumpwise in moving along the reaction line through the equilibrium point, which contradicts the dynamic equilibrium principle. Still larger constant variations are observed in the passage from one reaction line to another [3]. Naturally, the predictive ability of such models is fairly limited. In 1920-1930, de Donder suggested, as a continuation of Marcelin's studies, that reagent concentrations in the law of mass action should be replaced by their thermodynamic activities or fugacities to extend the range of the applicability of the law of mass action to nonideal systems [4, 5]. This suggestion, logical from the point of view of thermodynamics, did not find wide use in practical kinetic studies but initiated long-term discussion of the role played by thermodynamic activities in chemical kinetics and, generally, interrelation between kinetics and thermodynamics.

Let us consider the problem for the example of a reversible bimolecular reaction of the type A + B = C + D.

According to de Donder, the rate V of the process can be written as

$$V = V^{+} - V^{-} = k^{+}a_{\rm A}a_{\rm B} - k^{-}a_{\rm C}a_{\rm D}.$$
 (1)

Here, k^+ and k^- are the rate constants for the forward and back reactions and a_i is the thermodynamic activity of component *i*. This equation is consistent with the thermodynamic equilibrium condition, if we assume that the equation

$$k^{+}/k^{-} = \exp[(\mu_{A}^{\circ} + \mu_{B}^{\circ} - \mu_{C}^{\circ} - \mu_{D}^{\circ})/RT]$$

=
$$\exp(-\Delta G^{\circ}/RT) = \exp(A^{\circ}/RT) = K^{r}$$
 (2)

is fulfilled at equilibrium. Here, μ_i° is the standard chemical potential of component *i*, $-\Delta G^{\circ} = A^{\circ}$ is the standard chemical affinity of the reaction, $K^{\rm T}$ is the thermodynamic equilibrium constant, R is the gas constant, and T is the absolute temperature. Clearly, rate constant calculations according to de Donder require knowledge of component activity coefficients along the reaction line and the numerical differentiation of the experimental kinetic curve. The procedure is obviously laborious, which can only be balanced by the possibility of calculating the rate of the reaction at any composition point from several (ideally, single) experimental kinetic curves. This is what could not have been done. The problem is therefore the absence of any improvement in kinetic description if the obligatory requirement of consistency of thermodynamic and kinetic descriptions is introduced. More recently, as the thermodynamics of nonequilibrium processes has been developing, it became clear that (1) is not the only equation compatible with thermodynamics. In 1953, van Risselberg formulated a more general restriction imposed by thermodynamics on the rates of forward and back stages of a reversible chemical process [6]. This restriction had the form

$$-\Delta G = A = RT \ln(V^+/V^-). \tag{3}$$

Here, ΔG and A are already current (actual at the given time moment) rather than standard Gibbs energy and chemical affinity. It is easy to see that (3) is consistent with (1) if condition (2) is met. It, however, does not require (and does not presume) that k^+ and k^- should each be constant and allows activities in (1) to be replaced by affinities multiplied or divided by any values that are cancelled in calculating the V^+/V^- ratio. It is reasonable to introduce volume densities of thermodynamic activities for reactions of the type under consideration, namely, $[a_i] = a_i/U$, where U is the molar volume of the reaction mixture [3]. Equation (1) then takes the form

$$V = V^{+} - V^{-} = k^{+}a_{\rm A}/Ua_{\rm B}/U - k^{-}a_{\rm C}/Ua_{\rm D}/U$$

= $k^{+}[a_{\rm A}][a_{\rm B}] - k^{-}[a_{\rm C}][a_{\rm D}].$ (4)

The most important advantage of the volume densities of activities over activities as such is their transformation into usual molar concentrations in ideal systems. Equation (4) is an example of a modification of the classic Marcelin–de Donder equation acceptable from the point of view of thermodynamics. In this work, we inquire into its applicability to the description of the kinetics of reversible processes.

We do this for the example of acid-catalyzed esterification and transesterification reactions. The necessary conditions for kinetic curve measurements are combined in these reactions with the possibility of correctly calculating reagent activity coefficients. The experimental data on the kinetics of transesterification of *n*-butyl acetate with methanol were obtained by Panov and Garipova in 1990–1995 at the Faculty of Chemistry of St. Petersburg State University [7-10]. The kinetics of esterification of ethylene glycol with acetic acid was studied by the present authors. The procedure for chromatographically analyzing reaction mixtures was also described in [7–10], and the activity coefficients were calculated using the UNIFAC model and standard equations [11]. The geometric parameters of groups and intergroup interaction parameters for liquid-vapor equilibria were also taken from [11]. Molar density changes along reaction lines were ignored.

The rate constants for transesterification of butyl acetate were calculated in [7–10] from experimental data using the kinetic equation for reversible second-order reactions. The rate constants for the MeOH + BuAc stage at 298 K and [H⁺] = 1 M calculated from kinetic curves to the left and right of equilibrium were found to be 4.3×10^{-6} and 2.2×10^{-6} l/mol/s, respectively, which gave a difference of about two times. The

 $V^+ \times 10^4$, $V^- \times 10^4$, mol/(1 s)



Fig. 1. Butanol mole fraction dependences of (1, 2) V^+ and (3, 4) V^- for transesterification at 298 K; (1, 3) description according to the law of mass action for a second-order reversible reaction and (2, 4) calculations by (3) and (5).

results of the corresponding calculations are shown in Fig. 1. The V^+ and V^- values calculated by (3) are also shown. In order to obtain them, we first interpolated the experimental kinetic curves using polynomials third-order in time and then found the derivatives of concentration with respect to time at the corresponding points. The coefficients of the polynomials are listed in Table 1. After differentiation, the rate of the reaction was always divided by 10 and the analytic concentration of the catalyst, *p*-toluenesulfonic acid (*p*-TSA), to compare rates at equal *p*-TSA concentrations (0.1 M). It was proved in special experiments [7] that the rate of the reaction was proportional to the concentration of *p*-TSA. The chemical affinity was calculated as

$$A = -\Delta G = -RT\ln(K_x P_\gamma) + RT\ln P_a.$$
 (5)

Here, K_x is the concentration equilibrium constant and P_{γ} and P_a are the reaction products of the activity coefficients of the reagents in the equilibrium mixture and of reagent thermodynamic activities at the point of interest to us, respectively. Suppose that the V^+ and V^- values, activity coefficients, and thermodynamic equilibrium constants are known. We can then calculate the k^+ and k^- values by the modified Marcelin–de Donder equation (Eq. (4)), provided condition (2) is met. We found that these values decreased linearly along the reaction line. The approach that we used, however, did not presuppose them to be constant.

The authors of [7-10] experimentally studied the kinetics of the reaction over the whole central region of the tetrahedron of methanol-methyl acetate-butanolbutyl acetate system compositions. Proceeding as described above, we calculated 87 k^+ values and analyzed the composition dependence of this parameter. This dependence was found to be linear everywhere and can, at T = 298 K and [p-TSA] = 0.1 M, be

α ₀	A, mol/l	$B \times 10^{-4},$ mol/(1 s)	$C \times 10^{-9},$ mol/(1 s ²)	$D \times 10^{-14},$ mol/(1 s ³)	[<i>p</i> -TSA], mol/l	<i>R</i> _{corr}					
BuOH + MeOAc											
3:1	2.90	-0.820	1.28	-0.631	0.124	0.999					
1:1	5.97	-0.867	-0.385	4.88	0.108	0.999					
1:3	8.99	-0.823	1.30	-0.705	0.119	0.999					
MeOH + BuOAc											
3:1	0.145	1.81	-5.56	7.60	0.0497	0.999					
1:1	-0.24	2.54	-10.2	17.7	0.098	0.997					
1:3	-0.003	0.642	-0.854	0.238	0.055	0.999					

Table 1. Coefficients of interpolation polynomials for the kinetics of transesterification of methyl acetate and butyl acetate at 298 K, $K_x = [BuOH][MeOAc]/[MeOH][BuOAc] = 1.56$ (calculated from the data obtained in [7–10])

Note: Time is in seconds and concentrations in mol/l; α_0 is the initial alcohol : ester ratio.

described by the equation (correlation coefficient 0.953) [3]

$$k^{+} = 1.11 \times 10^{-6} + 4.24 \times 10^{-7} x_{\text{BuOH}} + 2.05 \times 10^{-6} x_{\text{BuAc}} + 1.94 \times 10^{-6} x_{\text{MeOH}}.$$
(6)

Here, x_i is the mole fraction of reagent *i*. Using this dependence and Eq. (4), we can easily calculate both the V^+ and V^- values and their difference. The results presented in Fig. 2 show close agreement with the experimental data. The physical meaning of the numerical coefficients of (6) becomes clear when this equation is rewritten in the more traditional form

$$k^{+} = A_1 x_{\text{BuOH}} + A_2 x_{\text{BuAc}} + A_3 x_{\text{MeOH}} + A_4 x_{\text{MeAc}},$$

where x_i is the mole fractions of the reagents ($\Sigma x_i = 1$). We then have $A_4 = 1.11 \times 10^{-6}$, $A_1 = 4.24 \times 10^{-7} + A_4 =$



Fig. 2. Butanol mole fraction dependences of V^+ and V^- for transesterification at 298 K; rate constant and rate calculations by (6) and (4), respectively; see Fig. 1 and Table 1 for conditions.

 1.53×10^{-6} , $A_2 = 2.05 \times 10^{-6} + A_4 = 3.16 \times 10^{-6}$, and $A_3 = 1.94 \times 10^{-6} + A_4 = 3.05 \times 10^{-6}$.

The A_i coefficients are simply the partial contributions of separate reagents to the rate constant. In its physical meaning, A_i is the rate constant for the reaction under consideration in the vicinity of the corresponding vertex of the tetrahedron of compositions. Note that direct rate measurements when one of the components is present in a large excess is a difficult experimental task. Another circumstance is also of importance. The result obtained is directly related to the proper selection of standard states for calculating activity coefficients. In the UNIFAC model, these states are pure substances, that is, the vertices of the composition tetrahedron themselves. It is the rate constants near them that enter into (6). This is no mere chance. Thermodynamics does not consider the mechanisms of reactions, and nonideality parameters should therefore be included with respect to such system states in which the reaction occurs by the same mechanism. In our problem, this requirement is met. If we selected a state in which the reaction does not occur at all as the standard state (for instance, the ideal gas state), the activity coefficients would contain contributions from processes that are not related directly to the kinetics of the reaction. Possibly, this is the reason why the earlier attempts at the introduction of activity coefficients into kinetic equations were unsuccessful.

Next, let us check the generality of the suggested approach for the example of reversible esterification of ethylene glycol with acetic acid. This system was selected because, first, this reaction occurs without stratification over a wide range of compositions including equilibrium and, secondly, reagent activity coefficients in alcohol–acid mixtures differ from one to a much greater extent than in the alcohol–ester system. Our aim was also to study the effect of the appearance of the second reversible stage.

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MODIFIED MARCELIN-DE DONDER EQUATIONS

Substance	c_0, \mathbf{M}	t^0 , s	A_1, M	<i>t</i> ₁ , s	<i>A</i> ₂ , M	<i>t</i> ₂ , s				
Hydrolysis, $[H_2SO_4] = 0.1 \text{ M}$										
Water	5.41902	2530.134	2.4608	12612.4715	1.2970	15276.7125				
Ethylene glycol diacetate	2.14113	3250.0	1.4405	10637.2323	0.6908	16659.8430				
Esterification, $[H_2SO_4] = 0.094 \text{ M}$										
Acetic acid	5.43968	0.0	2.6325	1361.08331	2.2407	7829.68691				
Ethylene glycol	1.27151	0.0	2.4479	1429.04068	0.9252	7277.01354				

 Table 2. Coefficients of interpolation functions for esterification–hydrolysis at 313 K

The reaction under consideration involves two reversible stages,

 $HO(CH_2)_2OH + AcOH = HO(CH_2)_2OAc + H_2O,$ $HO(CH_2)_2OAc + AcOH = AcO(CH_2)_2OAc + H_2O.$

The reaction was studied at an acetic acid-ethylene glycol or water-diethylene glycol molar ratio of 2 : 1 at 298–323 K in the presence of sulfuric acid as a catalyst. Ethylene glycol was purified by vacuum distillation at 110°C and 10 torr, and acetic acid was preliminarily distilled with a dephlegmator (30 cm) and frozen. Ethylene glycol diacetate was synthesized by the standard procedure for the preparation of esters described in [12] and purified by vacuum distillation with a dephlegmator (30 cm) at 95°C and 10 torr. The reaction mixtures were prepared gravimetrically on a VLR-200 balance and held at the temperature of measurements in a UTU-4 water thermostat. Reaction mixture composition was determined by gas chromatography on an LKhM-80 chromatograph with a heat conductivity detector. The conditions were a packed Teflon column ($4 \text{ mm} \times 5 \text{ m}$), 10% carbowax M on inerton, hydrogen as a carrier gas, 30 ml/min, column temperature 165°C, detector temperature 200°C, vaporizer temperature 200°C, and detector current 100 mA. The reagents left the column in the order water (W), acid (A), diacetate (D), ethylene glycol(E) + monoacetate(M).

In order to estimate the applicability of the law of mass action to a separate kinetic curve, we numerically integrated the system of equations

$$d[W]/dt = V_1 + V_2$$
$$d[D]/dt = V_2,$$

where $V_1 = k_1[E][A] - k_{-1}[M][W]$ and $V_2 = k_2[M][A] - k_{-2}[D][W]$ are the rates of the first and second reversible reactions. The k_1 , k_{-1} , k_2 , and k_{-2} values are related as $k_1/k_{-1} = K_1^r$, and $k_2/k_{-2} = K_2^r$, where $K_1^r = 2.67$ and $K_2^r = 0.8$ are the concentration equilibrium constants at 313 K of the first and second stages also measured experimentally. Calculations were performed by minimizing the total deviation of the theoretical curve from experimental. The function

$$F = \Sigma(\Sigma | c_i^{\exp} - c_i^{\text{theor}} |).$$

was minimized. Here, the external summation was over all five mixture components and the internal summation over all time moments at which measurements were taken. The k_1 and k_2 values were varied. The situation was found to be fully analogous to that with the transesterification reaction, we obtained an excellent description of all kinetic curves taken separately and a jumpwise change in the rate constant in passing through the equilibrium state. For instance, $k_1 = 2.9 \times 10^{-5}$ and $k_2 = 5.7 \times 10^{-6}$ l/(mol s) for esterification at 313 K and catalyst concentration 0.1 M. The same values calculated from the kinetic curves obtained under the same conditions were $k_1 = 1.35 \times 10^{-5}$ and $k_2 = 3.9 \times 10^{-6}$ l/(mol s).

Calculations of the rates V^+ and V^- and rate constants by (3) and (4) require experimental kinetic curves to be preliminarily differentiated. To do this, the experimental $c_i(t)$ dependences were interpolated using the Origin 5.0 program as

$$c_i = c_i^0 + A_1 \exp(-(t - t^0)/t_1) + A_2 \exp(-(t - t^0)/t_2).$$

For esterification, we interpolated the time dependences of the concentrations of acetic acid and ethylene glycol, and, for hydrolysis, those of water and diacetate. The interpolation coefficients are listed in Table 2. Note that the concentrations of the other reagents can be calculated from reaction stoichiometries and material balance equations if the initial composition is known. The calculation results are shown in Fig. 3. We see that an interesting phenomenon is observed for the first stage, namely, the rates of both forward and back reactions decrease as equilibrium is approached. No such effect was observed for transesterification. It can be explained by a decrease in the concentration of acetic acid, which is both a reagent and a catalyst. Naturally, (6) cannot describe this phenomenon. We therefore suggested a more complex relation. The partial rate constant was assumed to depend linearly on the mole fraction of acetic acid,

$$k_i = k_i^0 + k_{iA} x_A. aga{7}$$

The overall rate constant can then be written as

$$k = \Sigma (k_i^0 + k_{iA} x_A) x_i, \tag{8}$$

where the summation is over all five system components. Determining the mole fraction of monoacetate

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Fig. 3. Water mole fraction dependences of (1) V^+ and (2) V^- at the first stage of esterification at 313 K calculated by (3) and (5).

from the relation $x_{\rm W} + x_{\rm A} + x_{\rm E} + x_{\rm M} + x_{\rm D} = 1$ and substituting it into (8) yields

$$k = k_{\rm M}^0 + \Sigma (k_i^0 - k_{\rm M}^0 + k_{i\rm A}\delta_{i\rm A})x_i + x_{\rm A}\Sigma (k_{i\rm A} - k_{\rm M\rm A})x_i.(9)$$

Here, $\delta_{iA} = 1$ at i = A and $\delta_{ij} = 0$ otherwise. The coefficients of (9) can be found by the method of least squares through solving the system of linear equations obtained from nine conditions of the form $\partial E^2 / \partial H_k = 0$, where $E^2 = \Sigma (k_{exp} - k_{theor})^2$ is the sum of the squares of the deviations of the experimental rate constant values from those calculated by (9) and H_k denotes the sought

coefficients $(k_i^0 - k_M^0 + k_{iA}\delta_{iA}, k_{iA} - k_{MA}, \text{ or } k_M^0)$. The calculation results are shown in Fig. 4, and the coefficient values are given in the equation

$$k_{1}^{+} = -2.6 \times 10^{-9} + 1.3 \times 10^{-3} x_{W} + 1.5 \times 10^{-3} x_{A}$$

+ 7.9 \times 10^{-3} x_{E} - 4.5 \times 10^{-4} x_{D} - 1.9 \times 10^{-2} x_{W} x_{A} (10)
+ 1.1 \times 10^{-2} x_{A}^{2} - 3.8 \times 10^{-2} x_{A} x_{E} + 1.3 \times 10^{-2} x_{A} x_{D}.

In spite of a good description of the composition dependence of k^+ for both stages, the coefficients of (10) do not quite satisfy the physical meaning of the problem. Indeed, the closeness of k_M^0 to zero is hardly probable, and the negative $k_D^0 - k_M^0$ values are unlikely. This may be caused by the poor choice of interpolation equation (8) or the performance of calculations along one reaction line only. The validity of the latter remark is favored by the observation that both these values are not only negative but also close to zero in magnitude (compared with their analogues). In any event, the effectiveness of the suggested approach to the kinetics of reversible reactions in nonideal solutions was on the whole veri-



Fig. 4. Water mole fraction dependences of k^+ and k^- for the first stage of esterification at 313 K: (1) calculations by (3) and (4) and (2) interpolation according to (10); see Table 2 for conditions.

fied. The problems mentioned above will be studied in future experiments.

In conclusion, recall the main stages of the suggested procedure:

(1) Measurement of $c_i(t)$ kinetic curves at several reagent ratios on both sides of equilibrium.

(2) The determination of the concentration equilibrium constant K_x for at least one pair of mutually reversible reaction mixtures.

(3) The interpolation of kinetic curves by suitable $c_i(t) = F_i(t)$ functions and calculation of the $V_i(t_i) = dF_i(t)/dt$ rate at $t = t_i$.

(4) The calculation of reagent activity coefficients at experimental points with respect to the pure substances.

(5) The calculation of the thermodynamic equilibrium constant $k_p = K_x P_{\gamma}$.

(6) The separation of the rate of every reversible stage into V^+ and V^- according to the equation $\Delta G = -RT \ln(V^+/V^-)$.

(7) Rate constant calculation by the equation $V^{+/-} = k^+/-P[a_i]^{v_i}$.

(8) The interpolation of the composition dependences of $k^{+/-}$ and rate calculations at arbitrary compositions.

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