HYDROGEN OVERVOLTAGE ON MERCURY AT LOW CURRENT DENSITIES

IV. TEMPERATURE DEPENDENCE OF THE OVERVOLTAGE

UDC 541.13

L. I. Krishtalik

We studied the temperature dependence of the overvoltage of hydrogen generation on mercury during barrier-free discharge of hydrogen ions. We determined the actual activation energy and the actual preexponential multiple. There is put forward a theoretical calculation of the entropy of the activated complex during barrier-free discharge. We demonstrate the discrepancy between the theoretical and experimental preexponential multiple, which seems to be due to the approximate nature of the theory of absolute reaction rates. It is shown that knowledge of the activation energy for barrier-free discharge enables us to determine the adsorption energy for hydrogen on the cathode. We found the energy of the mercury/hydrogen adsorption bond to be 29 kcal.

The aim of the present paper is to study the temperature dependence of the barrier-free discharge rate for hydrogen ions. This dependence, interesting per se, also makes it possible to ascertain certain characteristics of the hydrogen generation process on mercury.

A procedure for the experiments and for purification of the materials that provides good reproducibility of the data was described in [1,2]. The temperature was maintained with an accuracy of ± 0.2°. Typical polarization curves obtained during one of the experiments are shown in Fig. 1. In Fig. 2 in the form of $\log i - 1/T$ we plot the temperature dependence of the reaction rate at a constant overvoltage for some of the solutions investigated by us (in each case we selected an exact value of the overvoltage falling at all temperatures within the region where the Tafel relationship $b \approx 0.06$ V is satisfied easily). The experimental points lie closely along the lines, which enables us to use them to find the activation energy of the discharge and the preexponential multiple. Data for all our experiments are grouped together in Table 1. This table, apart from the activation energy A_η, corresponding to a certain value of the overvoltage η, also shows the activation energy at the equilibrium potential $A_0 = A_\eta + \eta F$.

DISCUSSION OF RESULTS

The shape of the polarization curves is virtually identical for all temperatures. Just as at 25°, at all temperatures we observe that the overvoltage is not a function of the composition of the solution in the region corresponding to the bottom rectilinear segment, i.e., we observe a regularity typical of barrier-free discharge of hydrogen ions. The slope of the curves, as can be seen from Table 2, is close to the theoretical value 2.3 RT/F. The slight differences from the theory most likely falls within the limits of experimental error.

Let us consider the preexponential multiple during barrier-free discharge. To calculate preexponents by the transitional state theory we must, as is known, find the kinetic activity factor and the activation entropy. The first of these quantities was found by us earlier [2]. To calculate the entropy of the activated complex we used two distinct methods.

The first of these is similar to the one used earlier by Temkin [3]. Temkin started out from the analogy between transfer of a particle from a concentrated solution to a dilute one, and transfer of the particle from one solvent to another, and considered water at two close temperatures as two distinct solvents. According to Frumkin and Iofa [4], $RT \log \gamma^{\neq} \simeq \beta RT \log \gamma_{H_3O^+}$, i.e., $\Delta G^{\neq} \simeq \beta \Delta G^0_{H_3O^+}$, where γ is the activity coefficient, and ΔG is the variation in Gibbs standard free energy during transfer of the relevant particle from an ideal, infinitely-dilute solution to an actual, concentrated one. Taking it that this relationship also holds for transition from one temperature to another, and dividing it by ΔT and making ΔT tend to zero, we get

$$S^{\neq} \simeq \beta S^0_{H_3O^+}. \tag{1}$$

Similar arguments for barrier-free discharge based on the equality $\gamma^{\neq} \simeq \gamma_{H_2O}$ derived by us earlier [2] lead to the relationship

---

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 2, No. 10, pp. 1176-1184, October, 1966. Original article submitted October 12, 1965.

TABLE 1

Composition of solution	Temperature range, °C	Overvoltage η at which activation energy is determined, mV	Activation energy, kcal		log K
			at overvoltage η, A_η	at equilibrium potential, A_0	
3.1 KI+ 0,4HCl	10--50	440	12,6	22,7	$2{,}8_5$
4.1 KI+ 0,4HCl	25--50	460	12,0	22,6	2,7
4.2 KI+ 0,4HCl	10--60	470	12,3	23,1	3,0
4,2 KI+ 0,5HCl	25--60	470	13,2	24,0	4,0
4,3 KI+ 0,3HCl	10--50	450	11,4	21,8	2,1
4.3 KI+ 0,9HCl	25--60	460	12,4	23,0	3,0
5,2 KI+ 1,2HCl	25--60	460	13,5	24,1	4,0
5,6 KI+ 0,8HCl	25--60	460	11,0	21,6	$2{,}2_5$
6,0 KI+ $0{,}5_5$HCl	25--60	460	12,2	22,8	$2{,}9_5$
6 0 KI + 0,6HCl	25--50	460	13,0	23,6	3,6
6,0 KI+ 0,7HCl	25--50	475	13,3	24,2	4,3
3,0 KI+ 0,9HCl +		500	11,3	22,8	$2{,}8_5$
+ $1{,}3\cdot10^{-3}$ TBA	10--60	440	13,0	23,1	3,0
6,0 KI+ 0,4HCl +					
+ $1\cdot10^{-3}$ TBA	10--50	460	12,5	23,1	$2{,}7_5$
6.6NdBr + $0{,}8_5$	25--60	360	13,3	21,6	2,1
7NdBr + $0{,}8_5$HCl	25--60	400	13,8	23,0	$3{,}0_5$
11,8LiBr + 0,018HCl	25--60	410	12,9	22,3	2,3
11,8LiBr + 0,1HCl	10—50	460	12,4	23,0	2,9

TABLE 2

Temperature, °C	10	25	40	50	60
No. of experiments	6	31	13	13	10
Experimental b, mV	55,5	58	59,5	60,5	63,5
Theoretical b, mV	56	59	62	64	66

$$S^{\neq} \simeq S^{0}_{H_2O}. \tag{2}$$

A relationship of type (2) can be obtained by another method, without resorting to the approximate dependence mentioned above for the activity coefficients, or to the analogy between variation in temperature and solvent variable. Indeed, as pointed out in earlier papers [2,5], without barrier-free discharge, the activated complex coincides with the end state, i.e., with the adsorbed H atom and H_2O molecule. Hence

$$S^{\neq} = S^{0}_{H\,ads} + S^{0}_{H_2O\,ads} \tag{3}$$

$S^0_{H\,ads}$ only contains the oscillating component.

The oscillation frequency for the Hg–H bond can be evaluated with the help of an empirical rule linking frequency and bond energy [6]. The latter amounts to about 30 kcal, as will be shown later, which corresponds to the wave number $\nu \simeq 1100$ cm^{-1}. Hence, by using the known expression for the entropy of the harmonic oscillator (see, for example, [7]), we get $S^0_{H\,ads} \simeq 0.06$ eu, i.e., a quantity negligibly small compared with the second term in (3). Consequently,

$$S^{\neq} \simeq S^{0}_{H_2O\,ads} \tag{3a}$$

The variation in entropy during transition of the water from the body of the electrode to its surface can be found from the following arguments $\Delta G^0_{aH_2O}$ is equal to $N\cdot10^{-15}\,(\sigma_{Hg-H_2O} - \sigma_{Hg})$, where N is the Avogadro number, 10^{-15} is the area in cm^2 per molecule of water in the surface layer, σ_{Hg-H_2O} is the mercury/water surface tension, and σ_{Hg} is the surface tension of the mercury. Differentiating this expression with respect to the temperature, we find $\Delta S^0_{aH_2O}$. Applying the data for temperature dependence to the mercury's surface tension [8] and boundary tension at the maximum on the electrocapillary curve [9], we get $\Delta S^0_{aH_2O} = -1.15$ eu. There is some doubt as to how accurately this quantity relating to adsorption of the water at the zero-charge point potential describes the state of the water molecule formed through the H_3O^+ discharge. However, the order of magnitude is definitely correct,

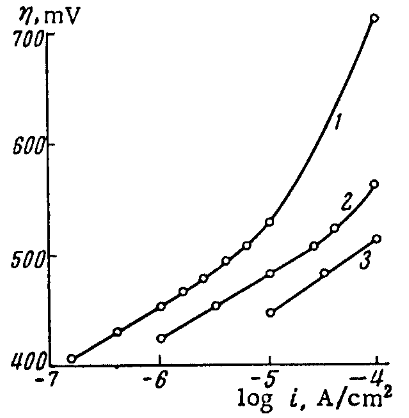

Fig. 1. Typical polarization curves for different temperatures (5.2 KI + 1.2 HCl): 1) 25; 2) 40; 3) 60°C.

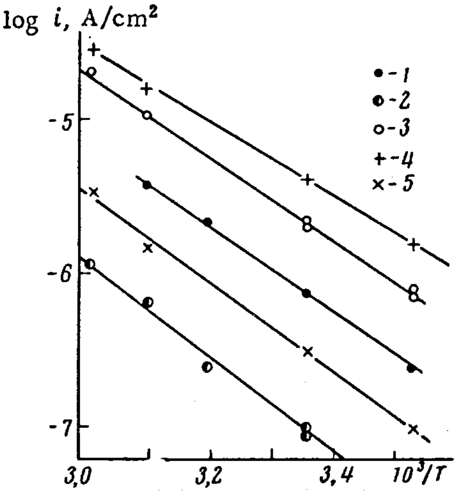

Fig. 2. Temperature dependence of current density i at constant overvoltage η for solutions of different compositions: 1) 11.8 LiBr + 0.1 HCl, η = 460 mV; 2) 7 NaBr + 0.85 HCl, η = 400 mV; 3) 4.2 KI + 0.45 HCl, η = 470 mV; 4) 3 KI + 0.9 HCl + 1.3 · 10^{-3} $N(C_4H_9)_4Br$, η = 500 mV; 5) same solution η = 440 mV.

and $\Delta S^0_{\alpha H_2O}$ is much smaller than $S^0_{H_2O}$ = 16.72 eu [10]. It follows from this that $S^0_{H_2O\ ads} \simeq S^0_{H_2O}$, i.e., we come back to the earlier quoted expression

$$S^{\neq} \simeq S^0_{H_2O}. \tag{2}$$

It was noted in [2] that relationships between the activity coefficients found experimentally for normal and barrier-free discharge can be generalized as

$$\gamma^{\neq} \simeq \gamma^{\beta}_{H_3O^+}\gamma^{\alpha}_{H_2O}. \tag{4}$$

Applying the same arguments as before to this generalized form, we get

$$S^{\neq} \simeq \beta S^0_{H_3O^+} + \alpha S^0_{H_2O}. \tag{5}$$

Equation (5) differs from Temkin's (1) as regards the term containing the water entropy. The expression for $\gamma^{\neq}$ used by Temkin as his initial one does not take into account the activity coefficient of the water, which in most cases is virtually unity. But if it is taken into account, we find an additional item in the expression for the entropy of the activated complex.

In reality, Eq. (5) means that the entropy of the activated complex is a quantity halfway between the entropies of the initial (H_3O^+ + e_{met}) and final (H_2O + H_{ads}) states (here we take it into account that $S_{e_{met}} \simeq 0$ and $S^0_{H\ ads} \simeq 0$). This deduction seems reasonable inasmuch as the activated complex corresponds to a certain configuration intermediate between the initial and final states. As is well-known, in the general case the entropy of the activated complex is not equal to the mean entropy of the initial and final states. But in the given case, as pointed out by Temkin [3] in regard to Eq. (1), the entropy items connected with oscillations in the covalent bonds are extremely small, and for practical purposes the entropy of the activated complex is determined entirely by its interaction with the solvent. But the latter (polarization of the dielectric, hydrogen bonds, etc.) proves to be halfway between the corresponding effects for H_3O^+ and H_2O. It is this fact that is shown in Eq. (5).

If we consider the entropy of the activated complex as the mean of two corresponding values for the initial and final states, it would be more correct to write down Eq. (5) as

$$S^{\neq} = \beta S^0_{H_3O^+ads} + \alpha S^0_{H_2O\,ads}. \tag{5a}$$

At α = 1 and β = 0 this equation becomes (3a), i.e., it turns into the expression derived directly for the entropy of the activated complex during barrier-free discharge.

For non-activation discharge, the transitional state coincides with the initial one, from which it follows directly that

$$S^{\neq} = S^0_{H_3O^+ads}. \tag{6}$$

But Eq. (6) may also be derived from (5a) at α = 0 and β = 1.

The fact that under limiting conditions Eq. (5a) gives us correct results obtained by an independent method suggests that the generalization of experimental data used to derive it is reasonable, and that (5a) may be applied as well to the case α = β = ½, i.e., to normal discharge.

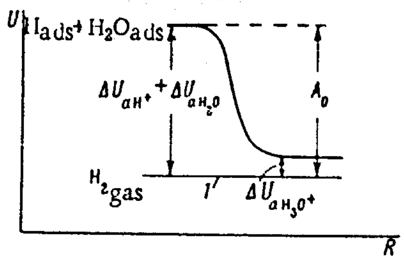

Fig. 3. Diagram showing profile of potential energy for barrier-free discharge of the ion H_3O^+ at equilibrial potential. ΔU_a is the adsorption energy of the corresponding particles; A_0 is the apparent actual activation energy at equilibrial potential. The horizontal line 1 marks the energy level for gaseous H_2.

Earlier [5], when the kinetic equation for barrier-free discharge was derived, the identity of the activated and finite states (entropy of the activated complex was determined by (3a)) was taken into account, but the value of the kinetic activity factor was not discovered [2].

When the relevant refinement has been made, the equation assumes the form (the relationship $\gamma_{H_2O}/\gamma_{H_2O\,ads}$ is taken as equal to unity)

$$i = \varepsilon \frac{kT}{h} \varkappa 10^{15} x_{H_2O} P_{H_2}^{1/2} (1 - \theta)$$

$$\times \exp\left\{-\frac{1}{RT}\left[\Delta H_{aH_2O} + \Delta H_{aH} + T\left(\frac{1}{2} S_{H_2}^0 - \Delta S_{aH_2O}^0\right) - \eta F\right]\right\}. \qquad (7)$$

Here ε is the electron charge, $\varkappa$ is the transmission coefficient, x_{H_2O} is the molar portion of water in the solution, θ is the coverage of the cathode surface by hydrogen, and ΔH_a represents the enthalpies of adsorption of the corresponding particles, while the remaining designations are conventional.

The actual energy activation A is determined from the slope of the curve $\ln i - 1/T$ at constant overvoltage [11].* The corresponding expression for A is obtained by differentiating (7)

$$A = -R\left(\frac{\partial \ln i}{\partial 1/T}\right)_\eta = \Delta H_{aH} + \Delta H_{aH_2O} + RT - \eta F. \qquad (8)$$

From (7) and (8) we find the actual preexponential multiple K

$$K = \varepsilon \frac{kT}{h} e \varkappa 10^{15} x_{H_2O} P_{H_2}^{1/2} (1 - \theta) \exp\left[-\left(\frac{1}{2} S_{H_2}^0 - \Delta S_{aH_2O}^0\right) \Big/ R\right]. \qquad (9)$$

Equation (9) enables us to calculate the preexponential multiple provided we take it, as is usually done, that the transmission coefficient is $\varkappa = 1$ (an adiabatic process). All the constants needed for this are known and the value of $\Delta S_{aH_2O}^0$ has been evaluated above (even if the error in evaluation is of the same order of magnitude, the inaccuracy introduced thereby into the calculation K is smaller than the experimental error). As a result of the calculation, we get log K = 5.7. The mean log K obtained from 17 independent experiments (see Table 1) is 3.0 (±0.4) (the mean square error is given in parenthesis).

Hence, there is a discrepancy between theory and experiment far beyond the limits of possible error.

Temkin [3] found the quantity log K = 2.6-3.3 (for two different solutions) from Iofa and Mikulin's data [12] for normal discharge; according to Post and Hiskey [13] log K = 4. In this way, for normal discharge the preexponential multiple is close to the value found by us for barrier-free discharge (the discrepancy is of the order of the experimental error).

Temkin's result for normal discharge [3] was log K = 5, and its concordance with the experimental figure was felt to be quite satisfactory. The slight discrepancy was ascribed, with certain reservations, to the effect of the tunnel passage of the proton. If, however, we use (5) or (5a) rather than (1), which Temkin uses, to calculate the preexponent, which now seems more valid, the preexponential multiple increases considerably and log K becomes equal to 6.7-6.8. When derived in this manner, K is an order larger than the theoretical value for barrier-free discharge.

And so both for normal as well as barrier-free discharge, we observe an appreciable difference between theory and practice. But we cannot explain this by the tunnel effect since in the case of barrier-free discharge there is no potential barrier through which the proton ought to pass. The tunnel effect might be manifested to some extent in normal discharge (the difference between theory and experiment would here be somewhat greater), but to draw fairly firm conclusions from the facts given does not seem to us to be possible.

---

*Just as comparison of i at different temperatures is made for a constant H_3O^+ concentration in the bulk and not on the surface, the activation energy determined this way is a so-called apparent quantity, i.e., it does not contain the term associated with the adsorption energy of the H_3O^+.

We should note that for barrier-free discharge at least, the discrepancy between theory and experiment is not due to the assumptions made when assessing the properties of the activated complex; we are not dealing here with a case in which an exact calculation is possible and we do not need to introduce additional assumptions. Hence, the reason for the discrepancy must evidently be sought in the approximations on which is based the theory of absolute reaction rates.

One such assumption might be that of the Maxwell-Boltzmann energy distribution for activated complexes [14,15]. A stricter quantum-mechanical derivation of the kinetic equation does not require this assumption, and all that is needed is observance of the Maxwell-Boltzmann distribution for initial particles [16]. The equation thus derived does contain a cofactor reminiscent in shape of ordinary expressions for a statistical sum, yet there is evidently no clear proof of its identity, considered in the theory of absolute rates, with the distribution function of the activated complex. Hence, exponential dependence on temperature including the height of the activation barrier can be considered fairly firmly justified, but the calculation of the preexponential multiple has a less reliable theoretical basis.

Similar conclusions can be reached on the basis of the statistical theory of the diffusion of particles through the potential barrier [17]. In this case, too, to obtain an exponential temperature dependence there must be equilibrial distribution only in the initial state, though not in the region of the barrier. Deviation from the equilibrial distribution at the top of the barrier results in reduction of the preexponential multiple.

In principle, it cannot be considered out of the question that the discharge of the hydrogen ions is to some degree nonadiabatic.

This may be due to peculiarities of the hydrogen adsorption bond. There may also be reduction of the transmission coefficient through curving or other features of the shape of the trough on the potential energy surface. The latter effects may be sensitive to the mass of the reacting particles [16], so that for this very reason the hydrogen reactions may not conform with the predictions of the absolute rate theory which usually describes the experimental data very well.*

In any event, the reaction involving cathodic generation of hydrogen is not the only one in which we observe a substantial difference between the theory and experiments. M. I. Temkin has drawn our attention to the work of Evzerikhin and Lyubarskii [19] in which they studied a chemical reaction with participation of adsorbed hydrogen — the catalytic hydration of benzene on nickel-cobalt and nickel-copper alloys. In this work they discovered a strong dependence (up to two orders) of the preexponential multiple on the composition of the alloy, which could hardly be explained without going beyond the range of the normal propositions of the theory of absolute rates.

The data contained in Table 1 gives us the mean activation energy for barrier-free discharge at an equilibrium potential $A_0 = 22.9 \pm 0.7$ kcal/mole. As can be seen from Eq. (8) (and from the potential curve diagram in Fig. 3), this quantity enables us to determine the hydrogen adsorption energy. Up till now it has not been possible to determine the latter experimentally because of the very low adsorbability of hydrogen on mercury.

Equation(8)contains $\Delta H_{a H_2O}$. It can be found from the data for $\sigma_{Hg - H_2O}$, and σ_{Hg} and their temperature dependence, used above to evaluate $\Delta S^0_{a\, H_2O}$. The value $\Delta H^0_{a\, H_2O} = -1.0$ kcal/mole; the error involved in determining this quantity is not of any importance in further deductions.

By using the experimental value of A_0 and the above evaluation of $\Delta H_{a\, H_2O}$ we can find $\Delta H_{a\, H} = 23.3$ kcal/g$\cdot$ atom. The error in determining this quantity hardly exceeds 2 kcal (considering that $\Delta H_{a H_2O}$ is determined with an accuracy of the active order of magnitude. By knowing the heat of adsorption of the hydrogen and its heat of dissociation [10], we can find the energy of the adsorption bond Hg—H. It was found to 29 kcal.

The literature contains a number of evaluations of the adsorption bond energy for hydrogen and mercury. Kobożev [20] took this value to be 6–8 kcal, basing himself on data on the dissociation energy of gaseous mercury hydride and on certain approximate calculations. The errors in his argument were pointed out in [21]. The bond energy found by us is considerably above the evaluation given by Kobozev. A value of $E_{Hg-H} = 29$ kcal makes any substantial contribution by "evaporation" of H atoms during removal of hydrogen from the surface unrealistic.

Another, extremely high value of E_{Hg-H} is given in papers by Bockris and fellow-workers [22,23]. They assumed the value to be close to 50 kcal. As far as we know, there has not been publication in detail of Low's data. In a recent papers by Nickolas et al. [24] it was demonstrated that provided there is thorough purification of all

---

*It is interesting to note in this connection that for D_3O^+ the preexponent is slightly larger than for H_3O^+ [18].

materials, the hydrogen has no effect on the surface tension of the mercury. Consequently, the bond energy of the adsorbed hydrogen and mercury is much less than 50 kcal.

Parsons and Bockris [22] concluded on the basis of model calculations of the discharge activation energy that $E_{Hg-H} > 40$ kcal, otherwise, in their opinion, the activation energy would prove too great compared with the experimental value. It should be noted that the activation energy as calculated by the intersection of potential curves method is fairly sensitive to the parameters of the model selected, hence it is hardly possible on the basis of these calculations to evaluate the boundary of permissible E_{Hg-H} so harshly. The calculation we made of the activation energy of the discharge is less sensitive to variations in the initial data since it was not the activation energy at an equilibrium potential that we calculated directly from the model, but the energy at the potential at which the potential curve minimums are all on the same level [6]. This quantity hardly depends at all on evaluation of the adsorption energy and furthermore, is quite small, about 8 kcal. Hence, the errors in calculating it from the absolute value are also rather small. The result of these calculations tallies with experimental data for an Hg—H bond energy of about 30 kcal, i.e., one coinciding with the experimental value obtained in the research in question. Without overestimating the accuracy of model calculations in the least, we feel we should stress that use of $E_{Hg-H} = 29$ kcal does not involve any inconsistencies in evaluation of the activation energy.

Frumkin, Bagotskii, and Iofa [21] found $E_{Hg-H} = 27$ kcal by comparing overvoltages on mercury and platinum. Although the mechanisms of hydrogen generation on these two cathodes are substantially different, the rate of the discharge process on platinum is closer in order of magnitude to the rate of the process as a whole [25], and for this reason the evaluation given in [21] is legitimate as a first approximation. This, in fact, explains why it conforms so well with the experimental value given above.

In [21] the assumption was expressed that the activation energy of the electrochemical desorption of hydrogen from a mercury cathode was tremendously small (the rough calculations were made on the assumption that it was zero). Since the adsorption heat we calculated for hydrogen amounted to 23.3 kcal, it is clear that the process of electrochemical desorption is very much exothermal. Hence, virtually unactivated occurrence is most likely. Model calculations by the method described above show that for mercury at all potentials of the cathode electrochemical desorption is nonactivational [26]. Its rate is sufficient for current flow right up to extremely high current densities, and at all overvoltages that can be studied in practice the recombination removal of hydrogen plays no part to speak of [5, 26]. The calculated coverage of the surface is very low, about 10^{-20} at equilibrium, and 10^{-5} at current densities of the order of 1 A/cm^2. This tallies well with data from capacitance and electrocapillary measurements, which show that coverage of the surface of a mercury cathode by hydrogen at any event is not greater than 10^{-4} (see, for example, [21]). A different picture would be observed at $E_{Hg-H} \gg 50$ kcal — activated electrochemical desorption, considerable participation of recombination and relatively high coverage of the surface by hydrogen, open to determination by electrochemical methods.

In conclusion we should like to express our appreciation to M. I. Temkin, Yu. A. Chizmadzhev, and R. R. Dogonadze for very valuable discussion of problems relating to the applicability of the theory of absolute reaction rates.

LITERATURE CITED

1. L. I. Krishtalik, ZhFKh, 39, 642 (1965).
2. L. I. Krishtalik, Élektrokhimiya, 2, 10 (1966).
3. M. I. Temkin, Tr. soveshchaniya po élektrokhimii, 1950, Izd. AN SSSR, Moscow (1953), p. 181.
4. Z. A. Iofa and A. N. Frumkin, ZhFKh, 18, 268 (1944).
5. L. I. Krishtalik, ZhFKh, 34, 117 (1960).
6. L. I. Krishtalik, ZhFKh, 31, 2403 (1957).
7. L. D. Landau and E. M. Lifshits, Statistical Physics [in Russian], Izd. "Nauka," Moscow (1964).
8. Landolt—Bornstein, Physik.-Chem. Tabellen, VI Ausg., Bd. II, T. 3, S. 421.
9. G. Gouy, Ann. chim. phys., (8), 9, 138 (1906).
10. Selected Values of Chemical Thermodynamic Properties, Natl. Bureau of Stand., Circular 500 (1952).
11. M. I. Temkin, ZhFKh, 22, 1081 (1948).
12. Z. A. Iofa and K. P. Mikulin, ZhFKh, 18, 137 (1944).
13. B. Post and C. F. Hiskey, J. Amer. Chem. Soc., 72, 4203 (1950).
14. S. Glesston, K. Leidler, and G. Éiring, Theory of Absolute Reaction Rates [in Russian], IL, Moscow (1948).
15. M. I. Temkin in book by N. N. Semenov, On Some Problems of Chemical Kinetics and Reactivity, Izd. AN SSSR, Moscow (1958).
16. G. Éiring, D. Wolter, and D. Kimball, Quantum Chemistry [in Russian], IL (1948).

17. Chandrasekar, Stochastic Problems in Physics and Astronomy, IL (1949).
18. B. Post and C. F. Hiskey, J. Amer. Chem. Soc., 73, 161 (1951).
19. E. I. Evzerikhin and G. D. Lyubarskii, Kinetics and Catalysis [in Russian], 5, 952 (1964).
20. N. I. Kobozev, ZhFKh, 25, 1111 (1951); 26, 112, 438 (1952).
21. A. N. Frumkin, V. S. Bagotskii, and Z. A. Iofa, ZhFKh, 25, 1117 (1951); 26, 1854 (1952).
22. R. Parsons and J. Bockris, Trans. Faraday Soc., 47, 914 (1951).
23. J. Bockris, Tr. IV Soveshchaniya po électrokhimii, 1956, Izd. AN SSSR, Moscow (1959), p. 53; B. Conway and J. Bockris, J. Chem. Phys., 25, 532 (1957).
24. M. E. Nickolas, P. A. Joyner, B. M. Tessem, and M. S. Olson, J. Phys. Chem., 65, 1373 (1961).
25. P. I. Dolin and V. B. Érshler, ZhFKh, 14, 886 (1940); P. I. Dolin, V. B. Érshler, and A. N. Frumkin, ZhFKh, 14, 907 (1940).
26. L. I. Krishtalik, ZhFKh, 33, 1715 (1959).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of the first issue of this year.
