

quantity ϵ_0 , but will be due to the incorrectness of this method of calculation. It is, of course, impossible to utilise values of ϵ_0 obtained in this way to calculate A' at different temperatures. However, these authors do so.

The first method proposed by Toropov and Brodskaya to calculate values of ϵ_0 at different temperatures consists in computing ϵ_0 from the expression

$$\frac{1}{\eta} \frac{d\eta}{dT} = \frac{4}{3} \frac{1}{p} \frac{dp}{dT} + \frac{1}{2T} - \frac{\epsilon_0 e^{\epsilon_0/RT}}{RT^2 (\epsilon_0 e^{\epsilon_0/RT} - 1)}, \quad (1)$$

obtained from my equation by taking logarithms and then differentiating on the assumption that A' and ϵ_0 can be regarded as constants. This condition is obviously unsuitable for deciding whether ϵ_0 depends on temperature, since it takes no account of the fact that A' is a function of temperature. In spite of this, however, the authors¹, using Eqn. (1), calculate the value of ϵ_0 for a given temperature and then, by substituting this value in the formula for the viscosity of liquids, obtain a value for A' . They thus use different values of ϵ_0 for different temperatures, contrary to the significance of this quantity. These values, as has already been stated, prove to be different for different temperatures because Eqn. (1) takes no account of the variation of A' with temperature.

If it is remembered that A' depends on temperature, taking logarithms and differentiating then yields not (1) but

$$\frac{1}{\eta} \frac{d\eta}{dT} = \frac{1}{A'} \frac{dA'}{dT} + \frac{4}{3} \frac{1}{p} \frac{dp}{dT} + \frac{1}{2T} - \frac{\epsilon_0 e^{\epsilon_0/RT}}{RT^2 (\epsilon_0 e^{\epsilon_0/RT} - 1)} \quad (2)$$

The appearance of the term $(dA'/dT)/A'$ in the right-hand side of Eqn. (2) has a substantial effect on the calculated value of ϵ_0 . The quantity A' is of the order of 10^{-5} – 10^{-6} , and therefore, even for small values of the derivative dA'/dT , the quantity $(dA'/dT)/A'$ will be quite large and cannot be neglected.

Eqn. (2) cannot be used to calculate ϵ_0 , since this would require not only A' but also the value of dA'/dT to be known. As stated above, the latter quantities cannot at present be calculated because of the lack of experimental data on the variation of the coordination numbers of liquids with temperature.

The second method employed by Toropov and Brodskaya for testing whether A' and ϵ_0 depend on temperature is also unsound. They suggest calculating values of ϵ_0 for different temperatures from the expression

$$\eta_1 p_2^{1/3} T_2^{1/2} / \eta_2 p_1^{1/3} T_1^{1/2} = (\epsilon_0 e^{\epsilon_0/RT_1} - 1) / (\epsilon_0 e^{\epsilon_0/RT_2} - 1), \quad (3)$$

obtained by writing my formula for two different temperatures and dividing one of the resulting expressions by the other on the assumption that A' is independent of temperature. But this condition makes Eqn. (3) useless for deciding whether ϵ_0 depends on temperature. It is necessary to remember that A' depends on temperature, so that Eqn. (3) must be rewritten

$$\eta_1 p_2^{1/3} T_2^{1/2} / \eta_2 p_1^{1/3} T_1^{1/2} = A'_1 (\epsilon_0 e^{\epsilon_0/RT_1} - 1) / A'_2 (\epsilon_0 e^{\epsilon_0/RT_2} - 1), \quad (4)$$

i.e. in the form of a single equation with three unknowns. It is obviously impossible to decide in this way whether or not ϵ_0 varies with temperature.

Eqns. (1) and (3) are thus unsuitable in principle for deciding the question of the dependence of ϵ_0 on temperature, and hence the conclusions reached by Toropov and Brodskaya on this basis are also incorrect.

Even the arithmetical work of these authors¹ is insufficiently correct. This can be seen from the Table, which

Substance	T, °K	Calc. by Toropov and Brodskaya		η		$\Delta\eta, \%$
		log A'	ϵ_0 , kcal/mole ⁻¹	calc.	expt.	
Hydrogen	15.39	3.291	0.0474	$9.14 \cdot 10^{-4}$	$2.00 \cdot 10^{-4}$	357
	18.95	3.867	0.0245	$8.87 \cdot 10^{-4}$	$1.43 \cdot 10^{-4}$	586
Stannic chloride	303.2	6.015	3.06	$8.75 \cdot 10^{-3}$	$1.43 \cdot 10^{-2}$	9
	333.2	5.684	0.88	$6.14 \cdot 10^{-3}$	$6.30 \cdot 10^{-3}$	1
Sodium nitrate	591.2	5.481	5.33	$16.02 \cdot 10^{-3}$	$2.78 \cdot 10^{-2}$	471
	681.2	5.382	5.61	$1.90 \cdot 10^{-2}$	$1.9 \cdot 10^{-2}$	0
Mercury	273.2	5.254	0.595	$1.92 \cdot 10^{-3}$	$1.08 \cdot 10^{-3}$	12
	463.2	4.539	0.05	$1.288 \cdot 10^{-3}$	$1.026 \cdot 10^{-3}$	25

gives viscosity coefficients calculated from my formula using values of A' and ϵ_0 calculated by Toropov and Brodskaya¹, experimental values of the viscosity coefficients, and the percentage deviation $\Delta\eta\%$.

If the calculation had been carried out correctly, the calculated values of the viscosity should have coincided with the experimental values, since it was from the latter that Toropov and Brodskaya calculated the values of log A' and ϵ_0 in the Table. Thus the reverse calculation shows the incorrectness of their calculations.

In the case of mercury A' and ϵ_0 cannot be calculated for a narrow temperature range since, owing to the fact that $\eta_1 p_2^{1/3} T_2^{1/2} / \eta_2 p_1^{1/3} T_1^{1/2} \approx 1$, the error in determining A' and ϵ_0 may be very great. Negative values for ϵ_0 and A' are not, of course, obtained. The fact that ϵ_0 and A' prove to be negative according to Toropov and Brodskaya's calculations is explained by their using a narrow temperature range and carrying out the calculations incorrectly.

SUMMARY

The methods of calculating A' and ϵ_0 employed by Toropov and Brodskaya to prove the dependence of these quantities on temperature cannot be accepted, and hence the conclusions reached on the basis of these calculations have no convincing justification.

1. A. P. Toropov and G. A. Brodskaya, *Zhur. Fiz. Khim.*, **34**, 1879 (1960) (preceding paper).
2. G. M. Panchenkov, *ibid.*, **24**, 1390 (1950).

Lomonosov Moscow State University

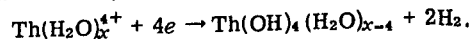
Received 10th March 1960

DISCHARGE OF LANTHANUM IONS AT A MERCURY CATHODE

Lyu Shou - zhun, G. M. Budov, and S. I. Zhdanov

Amalgams of lanthanum and several other rare-earth elements are usually obtained by electrolysis of alcoholic solutions of the anhydrous chlorides at a mercury cathode¹. There

is some indication² of the formation of lanthanum amalgam by the electrolysis of aqueous solutions, but the current efficiency is very low. At the same time, the opinion has been expressed³ that ter- and quadrivalent metals do not form amalgams at all on electrolysis of aqueous solutions of their salts. Mašek⁴ has put forward the idea that the polarographic waves observed in aqueous solutions of several metals of high valency (Th, Zr, Al, Be), previously attributed to the discharge of ions with the formation of amalgams, really represent the evolution of hydrogen from water molecules of the hydrate sheath, e.g. by the reaction



This point of view is shared also by Stradin' and Lepin'⁵.

Polarographic literature contains extremely contradictory ideas about the mechanism of the discharge of multivalent ions, including those of the rare-earth elements. Thus it has been concluded⁶ that Zr^{4+} ions are discharged to the metal at a mercury cathode in aqueous solutions, and formation of a deposit of metallic zirconium was said to be observed. In the opinion of Noddack and Bruckl⁷ amalgams are formed by the discharge of rare-earth ions from aqueous solutions at a dropping mercury cathode. Hamagushi et al.⁸ consider that the lanthanum wave with KCl or $(\text{CH}_3)_4\text{NCl}$ as supporting electrolyte represents discharge to the metal, whereas the yttrium wave corresponds to hydrogen evolution. The basis for this conclusion is the fact that gas bubbles are evolved from YCl_3 solutions, but not from LaCl_3 solutions. Treindl⁹ denies the possibility of reducing aqueous solutions of lanthanides to the metallic state at a mercury cathode. He regards the products of electrolysis as compounds of the type LaHX_2 , LaH_2X , and LaH_3 , where X represents a halogen.

A few papers have recently been published¹⁰ on the formation of amalgams by the electrolysis of aqueous solutions of salts of the rare-earth elements containing strong complexing agents, and it has been shown that amalgams can be obtained from these solutions with high yields.

Thus results in the literature indicate at least the difficulty of forming amalgams by the electrolysis of aqueous solutions of simple salts of the rare-earth elements. This is obviously to be explained mainly by the high activity of such amalgams, which readily evolve hydrogen from water, causing hydrolysis with formation of basic salts. Complex formation perhaps prevents hydrolysis and favours the formation of amalgams by keeping the metal in the dissolved state.

Analysis of the mercury phase during electrolysis should be of decisive significance in investigating the mechanism of the discharge of ions of multivalent metals. We have attempted to apply the method of labelled atoms to detect lanthanum in the mercury phase during the electrolysis of aqueous solutions of one of its salts with a mercury cathode.

Amalgams were prepared and their concentrations determined by a technique developed to measure the exchange currents at amalgams¹¹. Aqueous solutions of lanthanum chloride of different concentrations, labelled with the La^{140} isotope, were electrolysed in the upper cell. During electrolysis the solution and the mercury were stirred by means of a current of purified nitrogen. The cathode potential was maintained at -2.1 V (on the saturated-calomel-electrode scale). Electrolysis was not carried out at more negative potentials because of the copious precipitation of basic salts of lanthanum. The acidity of the solution was kept constant by periodically adding hydrochloric acid (twice redistilled) to the cell. After the passage of

about three times the amount of electricity required for complete deposition of the lanthanum, part of the mercury was run off into the lower cell without stopping the electrolysis. The tube through which the mercury overflowed was raised 6 mm above the bottom of the upper cell, which prevented the entry of active solution into the lower cell. The mercury was then treated with 0.1 N hydrochloric acid previously saturated with nitrogen. The mercury and the solution were mixed with a magnetic stirrer. A sample of the solution was periodically transferred to a cylindrical double-walled glass cell, which was slipped over a cylindrical glass Geiger-Müller γ counter; after the radioactivity had been measured, the sample was returned to the solution.

At low acidities of the solution (0.01 M) a potential of -2.1 V was reached at such a low current density that even electrolysis for 10-11 h gave no measurable concentration of lanthanum amalgam. At a solution acidity of 0.03-0.4 M, electrolysis of 0.1 M lanthanum chloride for 2-5 h yielded 10^{-4} - 10^{-2} M lanthanum amalgams. In more acid solutions the current density was so high that the solution was heated to boiling.

The absence of the formation of appreciable amounts of lanthanum amalgam in feebly acid solutions is very probably to be explained by the intense precipitation of basic salts under these conditions.

Thus these experiments show that, although discharge of lanthanum ions with formation of an amalgam does occur during the electrolysis of aqueous solutions of lanthanum chloride with a mercury cathode, the current efficiency is very low (< 0.1%), since the electricity is consumed mainly in the evolution of hydrogen.

1. "Inorganic Syntheses" (Translated into Russian), Vol. 1, Inostr. Lit., Moscow, 1951, p. 19.
2. B. S. Hopkins and L. F. Audrieth, *Trans. Amer. Electrochem. Soc.*, **66**, 135 (1934).
3. W. Kettembell, *Z. anorg. Chem.*, **38**, 213 (1904).
4. J. Mašek, *Coll. Czech. Chem. Comm.*, **24**, 159 (1959).
5. Ya. P. Stradin' and L. K. Lepin', *Izv. Akad. Nauk Latv. SSR*, No. 9, 97 (1958).
6. A. W. Laubengayer and R. B. Eaton, *J. Amer. Chem. Soc.*, **62**, 2704 (1940).
7. W. Noddack and A. Bruckl, *Angew. Chem.*, **50**, 362 (1937).
8. H. Hamagushi, J. Hashimoto, and Y. Narusawa, *J. Chem. Soc. Japan*, **80**, 43 (1959).
9. L. Treindl, *Coll. Czech. Chem. Comm.*, **24**, 3389 (1959).
10. D. I. Ryabchikov, Yu. S. Sklyarenko, and N. S. Stroganova, *Zhur. Neorg. Khim.*, **1**, 1954 (1956); **4**, 1985, 2682 (1959) [*Rus. J. Inorg. Chem.*, 1240 (1959)]; V. P. Shvedov and Fu I-bei, *Radiokhimiya*, **2**, 57 (1960).
11. V. V. Losev, *Dokl. Akad. Nauk SSSR*, **100**, 111 (1955); G. M. Budov and V. V. Losev, *ibid.*, **122**, 90 (1958).

Institute of Electrochemistry,
Academy of Sciences of the USSR

Received 5th April 1960