

ammonia decomposed must be present mainly in the oil produced, in the form of compounds of low volatility.

The velocity of reaction is independent of the ethylene pressure over a wide concentration range and of the ammonia pressure when light absorption is complete.

The temperature coefficient of the total process is determined by that of the photo-decomposition of ammonia.

The experimental results lead to definite conclusions with regard to the efficiency of various possible methods of producing saturated hydrocarbons from ethylene and atomic hydrogen.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 256]

## AN EFFECT OF THE BREADTH OF JUNCTION ON THE ELECTROMOTIVE FORCE OF A SIMPLE CONCENTRATION CELL<sup>1</sup>

BY GEORGE SCATCHARD AND T. F. BUEHRER

RECEIVED DECEMBER 8, 1930

PUBLISHED FEBRUARY 9, 1931

It is generally assumed that the electromotive force of a simple concentration cell, such as M, MX( $m_1$ ), MX( $m_2$ ), M, is independent of the method of making the junction between the two solutions, and that this fact has been demonstrated both theoretically and experimentally. The same theoretical argument may be extended to any cell involving a liquid junction to show that the electromotive force is independent of the thickness of the boundary layer provided that any element of the solution may be duplicated by taking  $x$  parts of the solution surrounding one electrode and  $(1 - x)$  parts of that surrounding the other electrode.<sup>2</sup> Such a boundary is known as a "mixture boundary" and is obtained in practice when the boundary is made without diffusion. A simple concentration cell must always give a "mixture boundary" regardless of diffusion.

The electromotive force of a cell with electrodes reversible to the  $k$ 'th ion, when the temperature and pressure are constant throughout the cell, is given by

$$E = \sum_{i=1}^n \int_B^A t_i dE_{ik} = \frac{RT}{F} \sum_{i=1}^n \int_B^A t_i d \ln \frac{(m_i \gamma_i)^{1/z_i}}{(m_k \gamma_k)^{1/z_k}}$$

where  $R$  is the gas constant,  $T$  the absolute temperature,  $F$  the faraday,  $t_i$  is the transference number of the  $i$ 'th type of ion,  $z_i$  is its valence (taken negative for a negative ion),  $m_i$  its molality, and  $\gamma_i$  its activity coefficient.<sup>3</sup>

<sup>1</sup> Presented before the Physical and Inorganic Chemistry Section at the Cincinnati Meeting of the American Chemical Society, September 10, 1930.

<sup>2</sup> P. Henderson, *Z. physik. Chem.*, 59, 118 (1907); 63, 325 (1908).

<sup>3</sup> P. B. Taylor, *J. Phys. Chem.*, 31, 1478 (1927).

A is the solution surrounding one electrode and B that surrounding the other.  $E_{ik}$  is the electromotive force of a cell without liquid junction with one electrode reversible to the  $i$ 'th ion, the other to the  $k$ 'th ion. Although the "individual ion activities" appear in the second part of the equation, their use is only formal for they appear in such a way that they may always be replaced by the mean activity of some salt, or by the difference in mean activities of two salts. This is shown sufficiently by the fact that in the first expression they are reduced to the electromotive forces of realizable cells. For a mixture boundary each  $m$ , and therefore the composition, is a function only of  $x$ . If the mobilities and activity coefficients are functions of the composition, independent of its gradient, they are also functions of  $x$ , and the integral is single-valued. That is, for any cell the electromotive force is independent of the thickness of the junction for a mixture boundary, and for a simple concentration cell it is independent of the method of making the boundary.

We believe that the flowing junction gives a "mixture boundary" not over 0.01 cm. in breadth, and that the Clark type of junction,<sup>4</sup> when properly made, also gives a "mixture boundary," but about 1 cm. broad. If so, they should give equal electromotive forces for any pair of solutions if the conditions given above are fulfilled. However, when one solution is saturated potassium chloride and the other 1 *M* hydrochloric acid, the difference between the two types of junction is about 0.5 mv.<sup>5</sup> We therefore undertook the study of a simple concentration cell to attempt to determine whether this is due to one type failing to give a "mixture boundary" or to a failure of real junctions to meet the other conditions of the thermodynamic equation. In a simple concentration cell it is not possible to obtain a difference in concentration comparable to that of the potassium or hydrogen ion in the above cell. We considered, however, that the cell Hg, HgCl, HCl ( $m_1$ ), HCl ( $m_2$ ), HgCl, Hg might give a measurable effect because of the large difference in the mobility of the ions. And we did find a small but indubitable effect.

### Materials and Apparatus

The measurements were made in the flowing junction apparatus previously described,<sup>6</sup> and the junction was allowed to increase in breadth by diffusion on standing after the flow was stopped. The calomel half-cells were the same as there pictured except that the end of the goose-neck arm was sealed off, instead of being constricted, and a hole about one millimeter in diameter was blown in the perpendicular side of the tube a few milli-

<sup>4</sup> W. M. Clark, "The Determination of Hydrogen Ions," The Williams and Wilkins Co., Baltimore, Maryland, 1928, p. 296.

<sup>5</sup> H. W. R. Biers, Thesis, M. I. T. (1927), confirmed by our own measurements.

<sup>6</sup> G. Scatchard, THIS JOURNAL, 47, 696 (1925).

meters from the end. The glass around the edge of this hole projected slightly, but not enough to prevent passing the tube easily through a rubber stopper. This simple device reduced considerably the entry of air bubbles into the goose neck. Of course, any dipping electrode should be used only where the solutions inside and out are the same.

The materials were prepared and purified as in the previous paper, except that each acid solution was boiled and cooled in a stream of nitrogen, and the composition was determined by a gravimetric chloride analysis; the calomel-mercury paste and the cell solutions were equilibrated for twelve hours on a shaking machine in an atmosphere of nitrogen, and introduced into the half-cells in the absence of air. These precautions were rather more harmful than helpful, for it was not found possible to keep oxygen excluded from such half-cells, with their openings often exposed to the air, so that the cells did not give a constant electromotive force over a period of days. The absolute values of the cell potentials are therefore uncertain to several tenths of a millivolt. Probably the variations during a day's run would also have been somewhat smaller without this precaution.

### The Results

Measurements were made with three sets of cells. The average results are given in Table I, where the first two columns give the concentrations of the two solutions in moles per 1000 g. of water; the third the average electromotive force in millivolts when the flow was stopped; the fourth gives the average increase of electromotive force, also in millivolts, when the solutions were flowing and the probable error of the average; the last gives the number of measurements of  $\Delta E$ . About half these measurements

TABLE I  
HYDROCHLORIC ACID CONCENTRATION CELLS AT 25°

$m_1$	$m_2$	$E$ (stop)	$\Delta E$ (flow)	No. of observations
7.29	0.1047	238.0	0.028 $\pm$ 0.005	22
7.29	.01117	331.0	.058 $\pm$ .019	17
1.091	.01117	194.7	.005 $\pm$ .019	6

were made on starting the flow and half on stopping it. For the latter the first measurements were made about one minute after the flow was stopped. Within the experimental error the change was complete within this time, and the electromotive force then remained constant for hours.

The averages are given to 0.001 mv. although the individual measurements were made generally only to 0.01 mv. and never beyond 0.005 mv. All conditions must be kept very constant to maintain the electromotive force of a cell constant to a hundredth of a millivolt. Perhaps our conclusions are better shown by a single run of somewhat more than six hours' duration when conditions were very good. The run was with the first cell, and  $E'$  is the observed electromotive force minus 237.00 mv. The values given are the minimum and maximum readings during a period of flow or of

TABLE II  
HYDROCHLORIC ACID CONCENTRATION CELL. RUN No. 6

Time from start		Flowing		Stopped	
Init.	Final	Min.	Max.	Min.	Max.
0	19	0.88	0.89		
20	204			0.85	0.86
205	229	.88	.88 <sub>6</sub>		
230	302			.84	.85
304	336	.89	.89		
338	368			.85	.85 <sub>6</sub>

cessation of flow. During six hours the value flowing varied only 0.01 mv. and that stopped varied only 0.02 mv. The difference between the minimum flowing value and the maximum stopped value is 0.02 mv. There can be no doubt of the reality of the effect.

From the Debye-Hückel interionic attraction theory we should expect that both the activity coefficients and the mobilities should depend slightly upon the concentration gradient, but we would scarcely expect to obtain a sufficient gradient in practice to show a measurable effect. There is another effect which should appear with much smaller gradients. Although the process is carried out in a thermostat, it cannot be isothermal. The mechanical mixing of the two solutions gives a heat effect and a resultant change of temperature in the boundary layer. These effects tend to be increased by the diffusion of ions through the boundary due to their Brownian motion. The temperature difference is dissipated, both along the axis of the tube and transversely to the walls, by the Brownian movement of all the molecules including those of the solvent. The temperature difference will be a complicated function of the concentration gradient and the time, and the effect on the electromotive force might be expected to be even more complicated and also to depend to a greater extent upon the ratio of the concentrations. Qualitatively the effect should depend upon the concentration as do our experiments. The fact that it disappears so rapidly shows that it must be very small except for a very steep gradient. Although the equation given above applies strictly to constant temperature, and therefore only to an infinitely wide boundary layer, the deviations must be immeasurably small for a breadth of even less than a millimeter.

Practically the effect of a sharp boundary in this cell is so small as to be negligible for all except the most precise work. Our results do show that a broad boundary, made by mixing rather than by diffusion if there are two electrolytes involved, should be preferable to a sharp boundary.

### Summary

The electromotive force of hydrochloric acid concentration cells was found to increase a few hundredths of a millivolt when the liquid junction was made very thin.

A probable cause is the change in temperature at the boundary produced by the heat of mixing of the two solutions.

CAMBRIDGE, MASSACHUSETTS  
TUCSON, ARIZONA

---

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

## THE ACTIVATION ENERGY OF ADSORPTION PROCESSES

BY HUGH S. TAYLOR

RECEIVED DECEMBER 13, 1930

PUBLISHED FEBRUARY 9, 1931

The rapid development, during the last decade, of the experimental study of adsorption phenomena at solid surfaces having catalytic activity has served to emphasize those adsorption processes in which a high degree of specificity is manifest. This work has centered attention on the operation of valence forces in determining adsorption and has indicated the existence of adsorption processes not markedly different from chemical reactions. The accumulation of experimental material has yielded, however, a number of data which, from the standpoint of classical adsorption theory, are abnormal. There has been considerable discussion of types of adsorption and distinctions drawn between "primary" and "secondary" adsorption.<sup>1</sup> In other cases there has been a tendency to speak of "reversible" and "irreversible" adsorption and to recognize only the former as conforming to true adsorption, to ignore the latter in the theoretical treatment of the subject. This latter attitude<sup>2</sup> undoubtedly arose from the lack of a general theory applicable to all types of adsorption. At the same time, owing to the orientation of experimental work, the data in conflict with the simplified theoretical treatment have grown so rapidly that it may now be stated that the experimental literature of adsorption dealing with the abnormal cases is now as extensive as that conforming to the simple theory. There are now numerous data showing abnormal variations in the extent of adsorption with both temperature and pressure, abnormal variations of the heats of adsorption with temperature and pressure, large variations in the velocity of attainment of equilibrium in different adsorption systems and in the velocity of evaporation of adsorbed gases inconsistent with present adsorption theory. Since these several factors in part determine the velocity of chemical processes at surfaces, the lack of a general theory covering such phenomena has resulted in an inadequate, and, in some cases, an incorrect treatment of the theory of chemical reactions at surfaces. It is the object of the present communication to point out the inadequacy of the classical theory of adsorption and

<sup>1</sup> Benton, *THIS JOURNAL*, 45, 887, 900 (1923).

<sup>2</sup> Hückel, "Adsorption und Kapillarkondensation," *Akademische Verlagsgesellschaft*, 1928.