Submitted to AIChE Journal

UCRL-19098
Preprint

RECEIVED
LAWRENCE
RADIATION LABORATORY
DEC 16 1969
LIBRARY AND
DOCUMENTS SECTION

CURRENTS LIMITED BY GAS SOLUBILITY

John Newman and Limin Hsueh

October 1969

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

UCRL-19098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Currents Limited by Gas Solubility

John Newman and Limin Hsueh

Inorganic Materials Research Division,
Lawrence Radiation Laboratory, and
Department of Chemical Engineering,
University of California, Berkeley

October, 1969

Abstract

The discrepancy between Šlendyk's polarographic limiting currents in 0.01 M HCl solutions and predictions of the effect of ionic migration is attributed to the formation of hydrogen gas at the electrode and the consequent perturbation of the convective velocity. Neglect of activity coefficient variations in the earlier calculations cannot account for the discrepancy. Diffusion coefficients of some gases in electrolytic solutions could conceivably be measured with an electrode at the upper end of a stagnant capillary by taking advantage of the limited solubility.

Introduction

An earlier work[1] treated the effect of ionic migration on limiting currents. The effect is particularly dramatic for the discharge of hydrogen ions from HCl-KCl solutions, where the limiting current may be enhanced by a factor of 3.34 over the diffusion limiting current for a growing mercury drop. The data of Šlendyk[2] provided confirmation of the calculations for 0.001 M HCl solutions with KCl concentrations ranging from 0 to 0.1 M. However, the data for 0.01 M HCl solutions with KCl concentrations ranging from 0 to 1 M deviated significantly from the theory.

The first attempt to resolve this discrepancy involved a refinement of the mass-transfer theory to account for the activity coefficients of the ions. In advance, one should not expect this explanation to be sufficient because the data for 0.001 M HCl solutions, which agree with the theory, involved ionic strengths as high as some of the 0.01 M HCl solutions, and the activity coefficients should be just as important.

A second, more plausible explanation for the discrepancy lies in the limited solubility of the hydrogen produced by the electrode reaction. This solubility is 0.000763 M for pure water at 25°C. An assumption of equal diffusion coefficients for H^+ ions and for H_2 would lead to a concentration of H_2 at the surface of 0.0005 M for the 0.001 M HCl solutions and an excess of KCl. This is just under the solubility limit, but with the more concentrated, 0.01 M HCl solutions, the solubility limit should be exceeded by a considerable amount.

For a growing mercury drop, the formation of hydrogen gas at the surface should effectively increase the stirring of the solution, thereby increasing the limiting current. Šlendyk's data

Table 1. Galvanometer deflections for limiting polarographic currents in HCl-KCl solutions, after Šlendyk.[2]

			0.001 M HCl			
KCl	0	-	0.0001	0.001	0.01	0.1
deflection[A]	58	-	46	29	19	14
			0.01 M HCl			
KCl	0	0.0001	0.001	0.01	0.1	1
deflection[B]	83	69	54	36	24	21
ratio	1.43	-	1.18	1.24	1.26	1.50

A Galvanometer sensitivity of 0.6 μA/mm.

B Galvanometer sensitivity of 6 μA/mm.

support this supposition since the current increased by more than a factor of ten for the same ratio of KCl to HCl, as indicated in table 1.

Activity Coefficients in Electrolytic Mass Transfer

The theory of electrolytic mass transfer in dilute solutions inherently assumes that the activity coefficients of all neutral combinations of ions are equal to unity. Since activity coefficients are strong functions of composition in electrolytic solutions, one might expect that a good first correction to dilute-solution theory should involve the activity coefficients. Thus the ionic flux might be written

$$\underline{N}_i = -\frac{c_i D_i}{RT}\nabla\mu_i + \underline{v}c_i \quad , \tag{1}$$

where μ_i is the electrochemical potential of species i. The first term on the right thus represents both diffusion and migration. In this first improvement over dilute-solution theory the diffusion coefficients D_i are taken to be constant and equal to their values at infinite dilution, and $\underline{v}$ can be regarded as the solvent velocity or a mass-average velocity. Equation 1 represents an approximation to the multicomponent theory appropriate to concentrated solutions in that it still neglects the friction interaction between solute species, as represented, for example, in the Stefan-Maxwell equation.

It is convenient, particularly in calculations, to introduce a quasi electrostatic potential Φ by the definition

$$\mu_n = RT\ln c_n + z_n F\Phi + \mu_n^{\theta} \quad , \tag{2}$$

where species n is a charged ion and μ_n^{θ} is a constant. It should be noted that the behavior of the potential Φ depends on the (arbitrary) choice of the ionic species n. By means of equation 2, it is now possible to express the first term in equation 1 in terms of the (measurable) activity coefficients of neutral combinations of ions:

$$\frac{c_i D_i}{RT}\nabla\mu_i = \frac{c_i D_i}{RT}\left[\nabla\mu_i - \frac{z_i}{z_n}\nabla\mu_n + \frac{z_i}{z_n}\nabla\mu_n\right]$$

$$= D_i\nabla c_i + D_i c_i \nabla\left(\ln f_i - \frac{z_i}{z_n}\ln f_n\right) + \frac{z_i F c_i D_i}{RT}\nabla\Phi \quad , \tag{3}$$

for uniform temperature. The equations describing the system thus become similar to those solved earlier[1] except for the inclusion of activity coefficients referred to species n and the use of the Nernst-Einstein relation $u_i = D_i/RT$ for the ionic mobility. For the activity coefficients of ions in moderately dilute solutions of several electrolytes, one can use, for example, the formulae of Guggenheim.[3] The numerical solution of the final set of coupled, ordinary differential equations is then complicated, but straightforward.[4] This approach to ionic mass transfer has been used in reference 10.

The results of such calculations for 0.01 and 0.001 M HCl solutions for a growing mercury drop are expressed in table 2 as the ratio of the limiting current to the value calculated by dilute-solution theory including the effect of migration, as outlined earlier.[1] The inclusion of the activity coefficients shows a small effect in each case, one which is not sufficient to account for the discrepancy in Šlendyk's data. It is of interest to note that the largest effect occurs in the solutions without KCl, the most dilute solutions. This is because the ionic strength is more nearly uniform in the presence of KCl, and consequently the activity coefficients vary less with position.

Table 2. For a growing mercury drop, calculated ratios of limiting currents to those calculated by dilute-solution theory.

$\sqrt{r}$	0.001 M HCl	0.01 M HCl
0.99504	0.99998	1.00065
0.95346	0.99962	0.99983
0.70711	0.99846	0.99650
0.30151	0.99636	0.99030
0	0.99514	0.98655

$r = c_{K^+}/c_{Cl^-}$ in the bulk solution.

The Limitation of Hydrogen Solubility

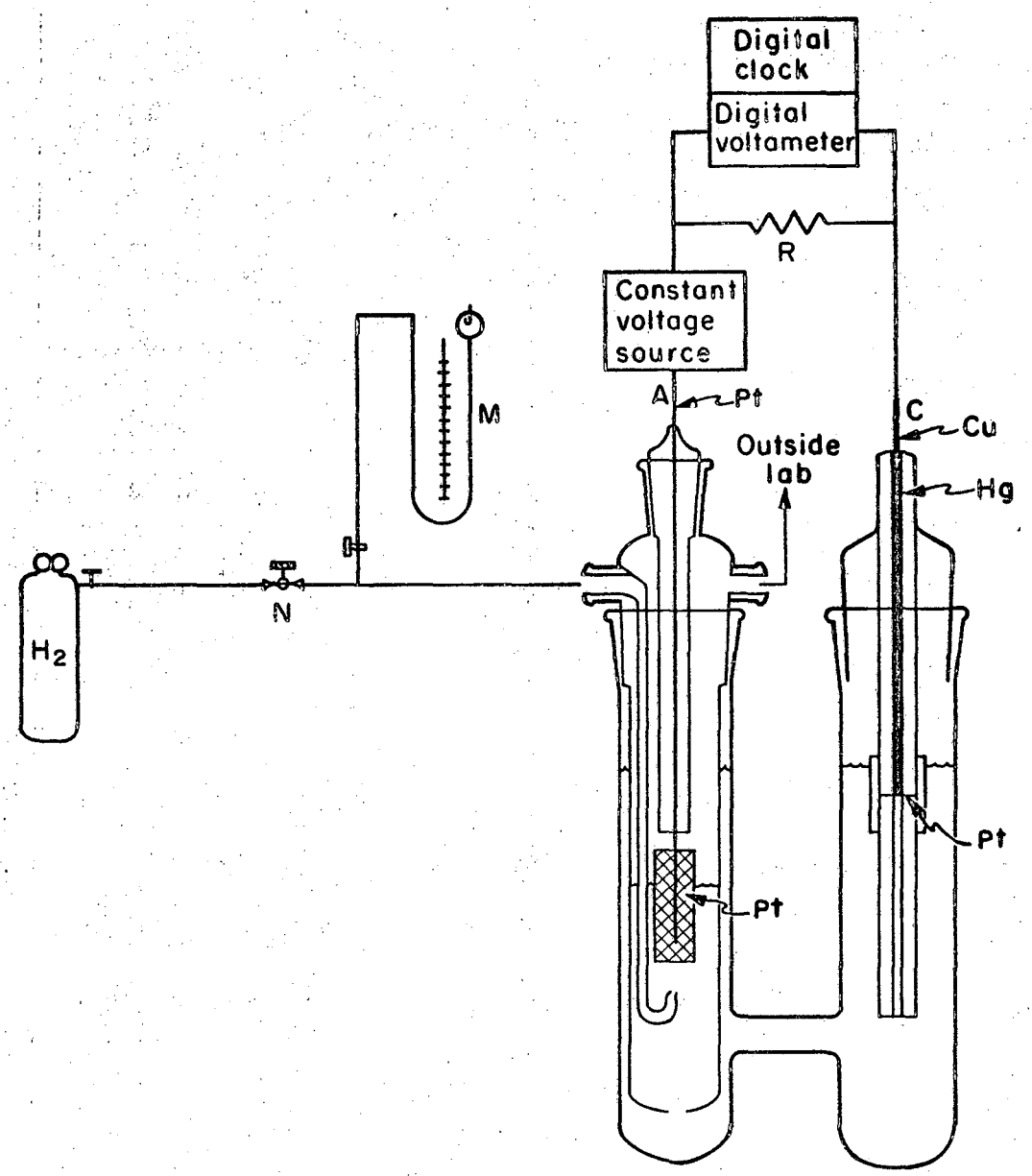
To test the hypothesis that hydrogen gas evolution in Šlendyk's 0.01 M HCl solutions enhances the convection and causes the discrepancy with the calculations of the effect of ionic migration, experiments were run with an electrode at the upper end of a stagnant capillary filled with solution and open at the bottom into a cell filled with solution (25°C) and containing the counter electrode. In the absence of extraneous stirring, the growing mercury drop and penetration into a stagnant fluid show essentially the same behavior.[1] However, in the capillary system used here, a gas blanket will cover the electrode when the solubility limit is exceeded, and the current should be effectively limited by the solubility of the gas produced in the electrode reaction. Furthermore, the current decreases inversely proportional to the square root of time, and there is assurance that the solution at the electrode surface is saturated, but not supersaturated.

The cathode was a platinum sheet sealed in a stagnant capillary (1.19 mm dia) with mercury as electrical contact, see figure 1. The anode was a platinum gauze hydrogen electrode. Lab grade cylinder hydrogen was used without further purification. The hydrogen pressure at the anode side was measured by an open end monometer (M) (Merian Fluid D-8325, density 1.75 used as meter fluid) and maintained at 1 inch pressure higher than atmospheric.

Solutions were prepared from reagent-grade potassium chloride and hydrogen chloride (specific gravity 1.191). The current flow through the cell was measured from the voltage drop across a known resistor ($R = 1000\Omega$) on a VIDAR-520 digital voltmeter, and the time was counted on a VIDAR-625 digital clock.

Some current vs. time curves are plotted on log scales and shown in figure 2. The slopes of most curves are slightly less than 0.5 (ranging from 0.45 to 0.50) and poor in reproducibility. They tend to be flat at large time, which we believe to be caused by the stirring of hydrogen gas formed within the diffusion layer.

For solutions of HCl (0.1 M) and KCl (ranging from 0.0191 M to 0.178 M) the observed values of $i\sqrt{t}$ (averaged over the time period where the current is inversely proportional to the square root of time) are shown in table 3. The measured values vary over a wide range from 0.194 to 0.46 mA-sec$^{1/2}$/cm^2. If this current were limited by transport of hydrogen ions to the electrode surface, the diffusion coefficients of H^+ would vary from 3.18 to 17.8 x 10^{-10} cm^2/sec, considerably below the accepted value of 9.31 x 10^{-5} cm^2/sec. On the other hand, if the



XBL 699-3834

Figure 1. Limiting current measurements in HCl-KCl solution with a stagnant diffusion cell.

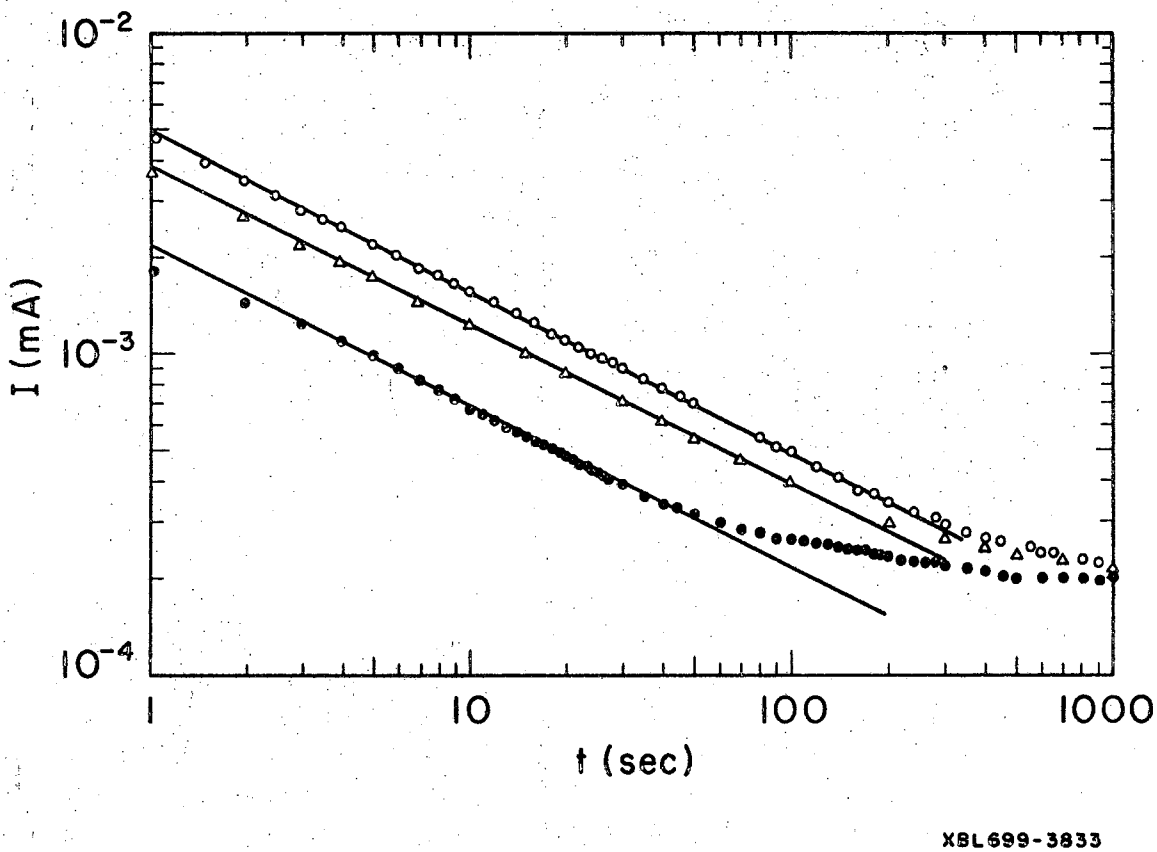


Figure 2. Limiting current curves of HCl-KCl in a stagnant diffusion cell at 25°C (● Run 1; o Run 6; Δ Run 8).

Table 3. Limiting current of HCl-KCl solution in a stagnant diffusion cell at 25°C.

Run #	HCl	KCl	Applied voltage	$I\sqrt{t}$	$i\sqrt{t}$
	M	M	V	10^{-3}mA $\sqrt{sec}$	$\frac{mA}{cm^2}\sqrt{sec}$
1	0.10	0.0333	0.418	2.18	0.196
2			0.418	2.16	0.194
6	0.10	0.0191	0.296	4.95	0.446
7			0.296	5.1	0.46
8			0.296	3.9	0.35
9			0.296	3.9	0.35
10			0.296	3.7	0.33
11			0.296	5.0	0.45
12			0.296	3.8	0.34
24	0.10	0.0568	0.200	3.9	0.35
25			0.253	2.6	0.234
26			0.200	3.08	0.278
31	0.10	0.178	0.205	3.5	0.315
32			0.181	3.4	0.306
33			0.181	3.2	0.388
34			0.181	2.25	0.292
35			0.181	2.8	0.252
36			0.181	2.65	0.24

solubility of hydrogen gas is taken to be 0.000752 M (the solubility[5] is lower than in pure water by 3.6% for 0.5 M HCl and by about 10% for 0.5 M KCl), the diffusion coefficient for dissolved hydrogen turns out to be 0.566 to 3.16 x 10^{-5} cm^2/sec. This is to be compared with the values of 4.09 (Tammann and Jessen[6]), 6.9 (Davidson and Cullen[7]) and 3.83 x 10^{-5} cm^2/sec (Aĭkazyan and Fedorova[8] at 23°C in 0.5 M H_2SO_4). Gubbins, Bhatia, and Walker[11] obtained a value of 3.79 x 10^{-5} cm^2/sec in 1 M KCl.

Discussion

The experimental results support the claim that the solubility of hydrogen is reached or exceeded for limiting currents at a dropping-mercury electrode or a stagnant-capillary electrode in HCl-KCl solutions for HCl concentrations greater than about 0.001 M. With an excess of KCl, one can refine the earlier estimate of the surface concentration of H_2 by multiplying by $\sqrt{D_{H^+}/D_{H_2}}$ to yield a value of 0.00076 M. The effect of migration can increase this by an additional factor of three. Although these values can be slightly greater than the solubility limit, one suspects, on the basis of the agreement with the calculated migration effect, that in Šlendyk's experiments with 0.001 M HCl solutions either the solution is supersaturated and no gas is formed or the convective velocity is not significantly enhanced by any gas which may be present. On the other hand, with 0.01 M HCl solutions the solubility limit is exceeded by more than a factor of ten, and the stirring is sufficient to cause the observed discrepancy.

Currents in a stagnant capillary limited by gas solubility can provide a method for measuring the diffusion coefficient of a gas dissolved in an electrolytic solution. For a reactive gas like hydrogen, it is probably better to use anodic limiting currents from a saturated bulk solution, as used by Aĭkazyan and Fedorova[8] on a rotating disk electrode, but the method may be useful for a gas like oxygen, where slow electrode kinetics can cause difficulties.[9] Care will be necessary to ensure that a uniform gas blanket will cover the electrode and paths of electrolytic conduction will be blocked.

Acknowledgment

This work was supported by the Petroleum Research Fund administered by the American Chemical Society and by the United States Atomic Energy Commission.

References

1. John Newman. "Effect of Ionic Migration on Limiting Currents." Industrial and Engineering Chemistry Fundamentals, 5, 525-529 (1966).

2. I. Šlendyk. "Polarographic Studies with the Dropping Mercury Kathode.--Part XXI.--Limiting Currents of Electrodeposition of Metals and of Hydrogen." Collection of Czechoslovak Chemical Communications, 3, 385-395 (1931).

3. E. A. Guggenheim. Thermodynamics. Amsterdam: North-Holland Publishing Company, 1959, pp. 357-361.

4. John Newman. "Numerical Solution of Coupled, Ordinary Differential Equations." Industrial and Engineering Chemistry Fundamentals, 7, 514-517 (1968).

5. William F. Linke. Solubilities. Volume I. Princeton: D. Van Nostrand Company, Inc., 1958.

6. G. Tammann and Vitus Jessen. "Uber die Diffusionskoeffizienten von Gasen in Wasser und ihre Temperaturabhängigkeit." Zeitschrift für anorganische und allgemeine Chemie, 179, 125-144 (1929).

7. J. F. Davidson and E. J. Cullen. "The Determination of Diffusion Coefficients for Sparingly Soluble Gases in Liquids." Transactions of the Institution of Chemical Engineers, 35, 51-60 (1957).

8. E. A. Aĭkazyan and A. I. Fedorova. "Opredelenie koeffitsienta diffuzii vodoroda elektrokhimicheskim metodom." Doklady Akademii Nauk SSSR, 86, 1137-1140 (1952).

9. R. E. Davis, G. L. Horvath, and C. W. Tobias. "The Solubility and Diffusion Coefficient of Oxygen in Potassium Hydroxide Solutions." Electrochimica Acta, 12, 287-297 (1967).

10. William H. Smyrl and John Newman. "Potentials of Cells with Liquid Junctions." The Journal of Physical Chemistry, 72, 4660-4671 (1968).

11. Keith E. Gubbins, Kamlesh K. Bhatia, and Robert D. Walker, Jr. "Diffusion of Gases in Electrolytic Solutions." A.I.Ch.E. Journal, 12, 548-552 (1966).

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720