[CONTRIBUTION NUMBER 46 FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF TENNESSEE]

The System Potassium Perrhenate–Potassium Chloride–Water

BY WM. T. SMITH, JR.

One of the methods for obtaining rhenium depends on the precipitation of potassium perrhenate by the addition of potassium chloride to water leachings of rhenium-bearing materials.[1] This investigation was undertaken in the interest of determining the most economical concentration of potassium chloride required for the precipitation which is commonly carried out at approximately 30°. It was also desirable to determine whether a practical increase in yield could be obtained by cooling the supernatant liquor to approximately 0°.

In practice the leach waters contain many other substances than those considered in this investigation, but they are variable, depending on the exact conditions of leaching and the composition of the material leached.

The solubility of potassium perrhenate in water has been reported previously.[2,3] While the values obtained by these investigators are in good agreement up to 50°, it was decided that the solubility at temperatures from 0 to 50° should be redetermined. The values obtained appear in Table I. There is good agreement with reported solubilities except for a 6% deviation[2] at 0°.

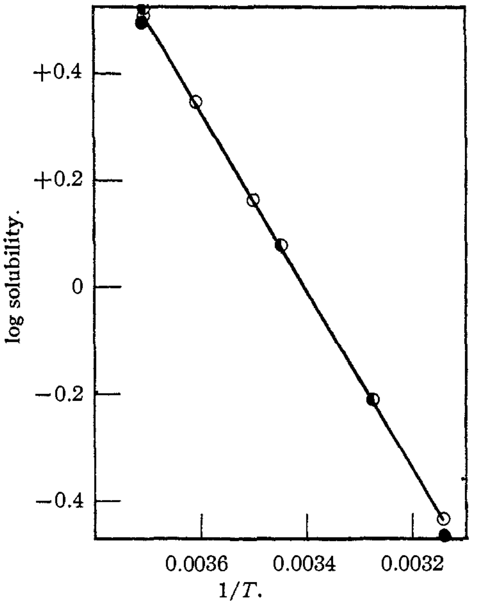

Fig. 1.—Plot of log solubility against the reciprocal of the absolute temperature; ●, Puschin and Kovac; ◐, Hölemann and Kleese; O, this investigation.

TABLE I

SOLUBILITY OF $KReO_4$ IN H_2O

Temp., °C.	g. $KReO_4$/100 g. H_2O
0.00	0.36
30.00	1.47
40.00	2.22
49.78	3.21

A plot of the logarithm of the solubility against the reciprocal of the absolute temperature gives a straight line (Fig. 1) from which the molar heat of solution, ΔH, is found to be 7630 cal.

The solubility of potassium chloride was determined at 0 and 30° as a check on the method used. Agreement with published values[4] was found.

The data for the three-component system potassium perrhenate–potassium chloride–water at 0 and 30° are presented in Tables II and III. The data indicate that 0.05 g. more potassium perrhenate can be recovered from 100 g. of water with 9.4 g. less potassium chloride when the precipitation is carried out at 0° rather than 30°.

TABLE II

THE SYSTEM AT 0°

Concn. in liq. phase, g./100 g. H_2O		
$KReO_4$	KCl	Solid phase
0.36	0.00	$KReO_4$
.027	9.51	$KReO_4$
.023	20.63	$KReO_4$
.022	28.05	$KReO_4$, KCl
.017	28.10	KCl
.007	28.04	KCl
.000	28.02	KCl

TABLE III

THE SYSTEM AT 30°

Concn. in liq. phase, g./100 g. H_2O		
$KReO_4$	KCl	Solid phase
1.47	0.00	$KReO_4$
0.423	1.63	$KReO_4$
.173	5.63	$KReO_4$
.114	13.84	$KReO_4$
.072	37.47	$KReO_4$, KCl
.000	37.42	KCl

Experimental

Materials.—The potassium perrhenate was purified and analyzed by Dr. A. D. Melaven of this Laboratory. On the basis of a rhenium analysis the sample was 99.8% potassium perrhenate.

The potassium chloride was Baker C. P. special grade, recommended for use in calomel electrodes.

The distilled water gave no test for chlorides and no detectible residue on evaporation.

Procedure.—The samples were placed in standard 8-inch Pyrex test-tubes equipped with air-driven circulating stirrers. The stirrers were made from 5-mm. glass tubing by blowing a hole in the tubing in such a way that it would tend to scoop up liquid when the tube was rotating in one

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(1) Feit, *Z. angew. Chem.*, **43**, 459 (1930).

(2) Puschin and Kovac, *Z. anorg. allgem. Chem.*, **199**, 369 (1931).

(3) Holemann and Kleese, *ibid.*, **237**, 172 (1938).

(4) "International Critical Tables," Vol. IV, p. 239.

direction. This hole was adjusted to a depth of about 0.5 cm. below the surface of the liquid. The lower 0.5 cm. of the stirrer was bent at an angle of 45 to 60°. The stirrer was run at such a rate (400 to 500 r. p. m.) that the excess solid in the tube was uniformly suspended in the liquid. Duplicate samples of the pure salts and the isothermally invariant mixtures were run. At temperatures above 0° one sample was started from a lower temperature while the other sample was heated well above the bath temperature before placing in the bath. The stirring tubes were maintained at a constant temperature in a water-bath controlled to $\pm 0.01°$. The time used for stirring and allowing the suspended solid to settle was varied, although one hour of stirring and one hour for settling was found to be sufficient. Four runs were made in which samples were withdrawn at half hour intervals after stirring was stopped. Duplicate samples of solution were withdrawn from each tube, one through a one inch, tightly packed, cotton plug and the other simply pipetted. No significant difference was found between the samples which were filtered and those which were not. Samples of the solutions were pipetted into deep, glass-stoppered weighing bottles. The samples were weighed, evaporated to dryness in an oven at 115–120° and the residues weighed. The residues which contained both potassium perrhenate and potassium chloride were analyzed for rhenium by a colorimetric method[5] using a wave length of 400 m. μ. on a Coleman Spectrophotometer. Check determinations on the solubility of potassium perrhenate at 0° were also made colorimetrically. Since the colorimetric method involves the addition of rather high concentrations of potassium thiocyanate and hydrochloric acid it was assumed that the presence of potassium chloride with potassium perrhenate would not interfere with the determination. The weight of potassium chloride was determined by difference. The solids in equilibrium with the solutions were not analyzed. The compositions of these solids were assumed on the basis that potassium chloride and potassium perrhenate are not isomorphous and that chloride-free potassium perrhenate is precipitated by the addition of potassium chloride to a solution of potassium perrhenate. No check determinations used varied more than 0.5% from the mean.

Summary

The solubility of potassium perrhenate in water has been determined from 0 to 50°. There is good agreement with published data with the exception of a deviation[2] of 6% at 0°.

The system potassium perrhenate–potassium chloride–water has been investigated at 0 and 30°. The advantages of recovering potassium perrhenate at the lower temperature are presented.

KNOXVILLE, TENN. RECEIVED AUGUST 2, 1945

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(5) Hiskey and Meloche, *Ind. Eng. Chem.*, *Anal. Ed.*, **12**, 505 (1940).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Fundamental Studies with the Dropping Mercury Electrode. IV. Empirical Modification of the Ilkovic Equation

BY JAMES J. LINGANE AND BRIAN A. LOVERIDGE

According to the Ilkovic equation the diffusion current constant, $i_d/Cm^{2/3}t^{1/6}$, of a given substance in a given supporting electrolyte should be a function of only the number of electrons associated with a molar unit of the electrode reaction, the temperature, and the diffusion coefficient of the reducible substance, and it should be independent of the characteristics (*i. e.*, $m^{2/3}t^{1/6}$) of the dropping electrode. However, it was demonstrated in a previous study[1] that the diffusion current constant of lead ion varies significantly and regularly with the value of $m^{2/3}t^{1/6}$, as shown by curve *a* in Fig. 1.

The rapid increase in $i_d/Cm^{2/3}t^{1/6}$ which occurs when $m^{2/3}t^{1/6}$ is increased beyond about 3.5 $\text{mg.}^{2/3}\text{sec.}^{-1/2}$ is not surprising. When $m^{2/3}t^{1/6}$ is large the drop time is necessarily quite small, and since rapid dropping causes stirring of the solution near the electrode, the normal diffusion layer is disturbed and transfer of the reducible substance to the electrode surface is accelerated.

On the other hand, the values of $i_d/Cm^{2/3}t^{1/6}$ also increase regularly with decreasing values of $m^{2/3}t^{1/6}$ below 3.5. The possibility that this left branch of the curve is simply a reflection of an instrumental peculiarity can be dismissed, because it was demonstrated that different methods of measurement with many different capillaries yield agreeing data and that the observed diffusion current is independent of the characteristics of the current-measuring galvanometer within wide limits.[1] Hence the left branch of curve *a* points to a real failure of the Ilkovic equation.

In the derivation of the Ilkovic equation[2,3,4] several simplifying assumptions were introduced. One of these is that the mercury drop is perfectly spherical throughout its life and that its entire surface is exposed to the solution; actually when the drop is very young an appreciable fraction of its area is screened off by the lumen of the capillary, and as the drop grows it loses its perfect sphericity and becomes very slightly tear shaped. These effects are observable in the motion picture photographs in Fig. 2 of a recent paper by MacNevin and Balis.[5] Therefore the average area is not exactly proportional to $m^{2/3}t^{2/3}$ as assumed.[4] It has also been assumed that the rate of mercury

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(1) J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **66**, 1425 (1944).

(2) D. Ilkovic, *Collection Czechoslov. Chem. Commun.*, **6**, 498 (1934); *J. chim. phys.*, **35**, 129 (1938).

(3) D. MacGillavry and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).

(4) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, 1941, p. 30 *et. seq.*

(5) W. M. MacNevin and E. W. Balis, THIS JOURNAL, **65**, 660 (1943).