Experimental Results

In the case of each compound, determinations were made at from twelve to fifteen different pressures over the range 10–760 mm. By plotting the logarithm of the vapor pressure against the reciprocal of the absolute temperature, an almost straight line relationship was obtained. The constants for the conventional equation

$$\log_{10} p_{\text{mm.}} = -(A/T) + B$$

were evaluated, and are recorded in Table II. Vapor pressures calculated by means of this equation fall within the limit of error of the experimental results.

Summary

1. The vapor pressure curves over the range 10–760 mm. have been determined for the following glycols: ethylene, 1,2-propylene, 1,3-propylene, 1,3-butylene and 2,3-butylene. With the exception of ethylene glycol, these data are here reported for the first time.

2. The densities and refractive indices are given for all the above compounds.

3. The methods used for the preparation of 1,3-butylene and 2,3-butylene glycols are also described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

The Mercury–Mercuric Oxide–Saturated Barium Hydroxide and Calcium Hydroxide Electrodes

BY G. J. SAMUELSON AND D. J. BROWN

It was the purpose of this research to study the mercury, mercuric oxide, barium hydroxide electrode with a view to its being used as a reference electrode. A saturated solution of the base was used to avoid troublesome preparation of standard solutions, thus permitting of easier preparation than is possible with the unsaturated type. Brown and Andrews[1] used Ming Chow's[2] electrode, containing sodium hydroxide, as a standard in their work and found its use very satisfactory.

The cell studied was, according to the common convention in designating it, as follows

$$\mathrm{Hg/(HgO(s),\ Ba(OH)_2(s)}/m\ \mathrm{KCl/KCl(s),\ Hg_2Cl_2(s)/Hg}$$

In the spontaneous reaction within the cell, an electron current flows in the external circuit from left to right, the complete reaction being

$$\mathrm{Hg + Ba(OH)_2 + Hg_2Cl_2 \rightleftharpoons 2Hg + BaCl_2 + HgO + H_2O}$$

Mercuric Oxide.—Mercuric oxide was prepared by decomposing pure mercuric nitrate. However, electrodes containing this oxide gave potentials not differing sensibly from those obtained with half-cells containing "chemically pure" commercial mercuric oxide.

Barium Hydroxide.—The best available grade of barium hydroxide was recrystallized from distilled water.

Potassium Chloride.—This was prepared by recrystallization of "chemically pure" potassium chloride from distilled water.

Mercurous Chloride.—Calomel was prepared electrolytically by the method of Lipscomb and Hulett.[3]

Agar-Agar.—This was an ordinary commercial form of the substance.

Water.—The water used was twice distilled, once from alkaline permanganate, Pyrex containers and a block-tin condenser being employed.

Electrode Vessels.—Electrode vessels similar to type to those of Lewis, Brighton and Sebastian.[4]

Reference Half-Cell.—A layer of mercury in the chamber was covered with a layer of electrolytically prepared calomel containing crystals of potassium chloride. Over this was poured a saturated solution of potassium chloride to within a few centimeters of the top of the chamber.

Experimental Half-Cells.—A flask containing water and excess barium hydroxide and mercuric oxide was shaken frequently, the contents of the flask being kept near the temperature at which measurements were to be made. This mixture was poured into the electrode chamber in which were a layer of mercury and additional barium hydroxide and mercuric oxide.

Half-Cell Chamber.—A glass jar, 6 cm. in diameter and similar to a hydrometer jar, was nearly filled with a saturated solution the same as that used in the electrode, excess of the solute being added. The jar was fitted with a large rubber stopper. The lower part of the long straight arm of an h-shaped glass tube passed through the large rubber stopper and dipped into the solution within the jar. The bent side-arm of the tube passed through a one-holed rubber stopper which was inserted into the mouth of the electrode vessel, the tube dipping beneath the surface of the solution in the vessel. The arrangement was such that the small stopper and h-tube suspended the electrode vessel in a position parallel to the jar, and on about the same

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(1) Brown and Andrews, THIS JOURNAL, **42**, 488 (1920).

(2) Ming Chow, *ibid.*, **56**, 388 (1934); **57**, 254 (1935).

(3) Lipscomb and Hulett, *ibid.*, **38**, 22 (1916).

(4) Lewis, Brighton and Sebastian, *ibid.*, **39**, 2245 (1917).

level, so that when the apparatus was immersed in the water-bath, the level of the water just reached the top of the jar and of the electrode vessel. The upper end of the longer straight arm of the h-shaped tube was closed with a short piece of rubber tubing containing a glass bead as a valve. Connection between the solution in the electrode vessel and that in the jar was effected whenever desired by sucking on the rubber tube at the upper end of the h-tube, the glass bead preventing the return of air and so making the solutions continuous.

Several such nests of four to eight electrodes each were made for both experimental and reference electrodes. Thus the electrodes could be checked against each other simply by connecting any pair of them to the potentiometer.

Baths.—Measurements on the electrodes were made at temperatures of 0, 15, 25 and 35 ± 0.02°.

Standard Cell.—A Weston standard cell recently calibrated by the Bureau of Standards.

Potentiometer.—All potential measurements were made with a Leeds and Northrup Type K potentiometer calibrated by the Bureau of Standards and equipped with a Type R reflecting galvanometer.

Salt Bridge.—Several methods of effecting contact between the saturated solutions of barium hydroxide in the one electrode and of potassium chloride in the reference electrode were tried.[5] Finally the gel–salt bridge method was adopted. The bridge used in this work consisted of a gel of 2.5% agar–agar in molar potassium chloride solution.

Several bridges were tried in every set of measurements to establish the reproducibility and constancy of the agar–salt bridge. Table I gives representative data for the cell

$$Hg/HgO(s),\ Ba(OH)_2(s)/bridge/KCl(s),\ Hg_2Cl_2(s)/Hg$$

at 25° with four changes of the agar–salt bridge, the time elapsed from insertion of the bridge being also indicated in hours and electromotive force in volts. The same combination of half-cells was used with all of these bridges, the different bridges being used successively.

TABLE I

AGAR BRIDGES WITH SAME CELL

	Bridge 1		Bridge 2
Time	E. m. f.	Time	E. m. f.
0	0.0965	0	0.0972
2½	.0975	5	.0979
15	.0982	21	.0981
23	.0982	95	.0980
64	.0981		
	Bridge 3		Bridge 4
0	0.0984	0	0.0982
4	.0985	1	.0984
18	.0985	7	.0985
30	.0985	23	.0984

From these data it appears that the whole cell, which includes the reference and experimental electrodes and the agar–salt bridge, becomes relatively constant within a short time after insertion of the bridge, and for an indefinite period of time.

Before comparison of the experimental half-cell with the reference electrode was made, it was customary to check the latter against the other members of the reference nest (consisting of four saturated calomel electrodes, an occasional exchange of one of these for a freshly prepared one being made). At all times the maximum variation between the various calomel half-cells used was within 0.1 millivolt. These were found also to be very nearly constant and reproducible if made of highly purified materials exactly as directed.

The usual procedure with the experimental electrodes was to compare the several ones with one another, Table II, and to compare only one of these with the reference half-cell.

TABLE II

E. M. F. COMPARISON OF BARIUM HYDROXIDE HALF-CELLS

	Hours			
Cell	1	18	42	87
2–6	0.00018	0.00019	0.00019	0.00019
3–6	.00007	.00010	.00007	.00007
4–6	.00004	.00004	.00005	.00005
5–6	.00013	.00011	.00011	.00011
3–4	.00005	.00004	.00004	.00004

The first column indicates the half-cell combination read, the electrodes being numbered, the one on the left being negative to the one on the right. The potential differences in volts are given at the indicated time elapsed from the insertion of the nest of electrodes in the bath.

These half-cells, when measured against the reference electrode, gave values, from the beginning of the period of measurement to the end, which were more nearly constant than the bridge itself. From Table II it may be seen that the barium hydroxide half-cells reached almost at once, and maintained for indefinite periods of time, steady relationship with each other. Moreover, the greatest difference between any pair of the freshly prepared half-cells containing purified substances is less than 0.2 millivolt. A summary of data for representative determinations on electrodes of the type mercury-mercuric oxide-saturated barium hydroxide, where the material used were of the highest quality available, is given in Table III.

This electrode is negative to the saturated calomel electrode, according to convention, and since the latter has been established as ±0.2446 volt

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[5] Lamb and Larson, THIS JOURNAL, **42**, 229 (1920); Ferguson and co-workers, *ibid.*, **54**, 1279 (1932); Guggenheim, *ibid.*, **52**, 1331 (1930).

TABLE III

CELLS, Hg/HgO(s), $Ba(OH)_2(s)//KCl(s)$, $Hg_2Cl_2/(s)Hg$

T., °C.	Electrodes	Period of meas. days	Max. deviation, v.	Av. e. m. f. as read, v.	Av. e. m. f. *vs.* cal. at 25°	Temp. coefficient volts deg.
0	6	5	0.0004	0.0794	0.0844	−0.00052
15	6	5	.0002	.0902	.0922	− .00062
25	6	16	.0003	.0984	.0984	− .00062
35	5	18	.0002	.1066	.1046	

at 25° in comparison with the normal hydrogen electrode,[6] the former may be seen from Table III to have a value of +0.1562 volt at 25° against the hydrogen electrode. With an increase in temperature, the mercuric oxide–saturated barium hydroxide electrode becomes more negative to the calomel electrode and so less positive to the hydrogen electrode by 0.00060 volt per degree. Hence, the true potential of the electrode against the normal hydrogen electrode is given by the expression

$$E_t = 0.1462 - 0.00060(t - 25°)$$

A number of rapid exchanges from one bath to another were tried on this electrode to establish the effect of a sudden change of temperature on its potential. In all of these, whether the temperature change was positive or negative, the electrode assumed potentials within an hour which varied not more than 0.0003 volt from those of the ones already in the bath.

It has been seen from the data in Table II, which are representative of those obtained for various determinations, that the experimental electrode under investigation attained equilibrium very rapidly and then was almost constant in potential for an indefinite period of time. This was found to be the case whether chemically pure or further purified materials were employed in its preparation. The electrode was very easily prepared. A mixture of the oxide, barium hydroxide and water, shaken for a few minutes to ensure saturation, and then poured over a layer of mercury in the half-cell chamber constituted an electrode the potential of which, within an hour after it was placed in the bath, was not sensibly different from that of another prepared by mechanically shaking the mixture for several hours, or by occasionally agitating it for several days.

The electrode was readily reproducible in potential value when made of the purest materials. However, with the less pure materials the potentials, though constant to within 0.0002 volt for any half-cell were noticeably different for various half-cells from those obtained when the purest materials were used. In all the electrodes of ordinary "chemically pure" barium hydroxide and mercuric oxide, red and yellow, secured from various sources, and once-distilled water that were studied, the potentials were within a maximum variation of ±0.001 volt of those attained by electrodes of repurified materials.

The Mercury, Mercuric Oxide, Saturated Calcium Hydroxide Electrode

Other factors influencing the electromotive forces of the half-cells being constant, the mercury–mercuric oxide electrode containing saturated calcium hydroxide should have a temperature coefficient less negative than that of the one containing saturated barium hydroxide.

The study of the mercury, mercuric oxide, calcium hydroxide electrode was carried out, in general, in the same manner as that of the barium hydroxide electrode. The calcium hydroxide was prepared from pure calcium carbonate. Pure sodium carbonate and calcium chloride were allowed to react and the carbonate was filtered, washed free of chlorides and calcined until no carbonate remained. The resulting oxide was then used in the half-cell. The Hg/HgO(s) Ca(OH)(s) electrode is negative to the saturated calomel electrode. From the table the electromotive force of the mercury–mercuric oxide–saturated calcium electrode at 25° is −0.0523 volt against the saturated calomel at 25°. Accordingly, it should have a value of +0.1923 volt against the normal hydrogen electrode at that temperature. With an increase in temperature the electrode becomes less negative to the saturated calomel electrode at 25° by 0.00010 volt per degree.

CELLS, Hg//HgO(s), $Ca(OH)_2(s)//KCl(s)$, $Hg_2Cl_2/(s)Hg$

T., °C.	Electrodes	Period of meas. days	Max. dev., v.	Av. e. m. f. as read v.	Av. e. m. f. *vs.* cal. at 25°	Temp. coefficient volts/deg.
0	8	2	0.0022	0.0497	0.0547	+0.00010
15	7	3	.0014	.0512	.0532	+ .00009
25	12	7	.0018	.0523	.0523	+ .00010
35	10	7	.0016	.0533	.0513	

In the most extreme cases the agar–salt bridge showed a reproducibility, with the calcium hydroxide electrodes, which was within ±0.0010 volt—not as good as with the barium hydroxide

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(6) Ewing, THIS JOURNAL, **47**, 301 (1925).

electrodes. However, the mercury, mercuric oxide, calcium hydroxide electrodes compared very favorably in speed of reaching equilibrium and in constancy with those containing barium hydroxide. It may be seen from the table that the maximum deviations between the electrodes read at the various temperatures is considerably greater than with the barium hydroxide half-cells, reaching a maximum of about two millivolts. This was the usual situation with these half-cells. A number of electrodes were made up using ordinary materials, "technical" calcium oxide, ordinary C. P. red and yellow mercuric oxide, etc., and these were found to give potentials usually well within ±0.002 volt of the above value.

Summary

1. The electrode $Hg/HgO(s)$, $Ba(OH)_2(s)$ has been studied from the standpoints of ease of preparation, constancy, reproducibility and effect of temperature change.

2. The potential of the electrode including a liquid junction, compared to the hydrogen electrode at zero is $+0.1462 - 0.00060(t - 25°) \pm 0.0002$ volt.

3. Likewise the potential of the electrode using ordinary materials is $\pm 0.1462 - 0.00060 (t - 25°) \pm 0.001$ volt.

4. The electrode using ordinary materials is very satisfactory for ordinary work.

5. The electrode $Hg/HgO(s)$, $Ca(OH)_2(s)$ has been studied from the standpoint of ease of preparation, constancy, reproducibility and temperature coefficient.

6. The potential of the electrode against the normal hydrogen electrode is $+0.1923 + 0.00010 (t - 25°) \pm 0.0010$ volt.

LINCOLN, NEBRASKA RECEIVED JULY 29, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, UNIVERSITY OF TORONTO]

The Diffusion of Helium through Fused Silica

BY E. O. BRAATEN AND G. F. CLARK

Introduction

It has been established by many observers[1] that the lighter gases can diffuse readily through fused silica. Over a wide range of temperatures and pressures it has been found that the rate of diffusion is proportional to the pressure, and that the diffusion process has a temperature coefficient expressed by an exponential relation (equation 1). Most of the results have been obtained at high temperatures where rates of diffusion are larger and experimental procedure less tedious. Sufficient data are not yet available at the lower temperatures to permit of construction of a theory valid over the whole temperature range where diffusion occurs.

Theory

It has been shown that when the Lennard-Jones[2] theory for diffusion is applied to systems of inert gases in silica the resulting equations do not fit experimental results. It appears, therefore, that the diffusion of monatomic gases through silica does not involve the mechanism of surface adsorption followed by subsequent diffusion. An extension of the theory was made by Alty,[3] who postulated that the gas enters the solid directly from the gas phase after which it penetrates the solid in the manner described by Lennard-Jones. Before the gas can enter the cracks in the solid it must have an energy, W_0, sufficient to overcome a potential barrier composed of two overlapping fields at the entrance to each pore, a comparatively small energy E_0 being also required for the atom to diffuse along the cracks.

The diffusion equation which Alty derived is

$$M = Bp\, e^{-(W_0 + E_0)/kT} \qquad (1)$$

where $E_0 \ll kT$, p is the pressure, M is the mass flowing through the solid per unit time, k is Boltzmann's constant, B is a constant, and T the absolute temperature. Equation (1) is found to be valid for temperatures above 200°, but below this temperature the rates are higher than would be expected according to the equation. Barrer[4]

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(1) P. Villard, *Compt. rend.*, **130**, 1752 (1900); A. Jacquerod and F. L. Perrot, *ibid.*, **139**, 789 (1905); E. C. Mayer, *Phys. Rev.*, **6**, 283 (1915); G. A. Williams and J. B. Ferguson, THIS JOURNAL, **44**, 2160 (1922); Johnson and Burt, *J. Opt. Soc. Am.*, **6**, 734 (1922); Steacie and Johnson, *Proc. Roy. Soc.* (London), **117A**, 662 (1927); J. W. McBain, "The Sorption of Gases by Solids," Geo. Routledge & Sons, Ltd., London, 1932, where a complete bibliography is given up to the date of publication; *Trans. Faraday Soc.*, "A General Discussion on the Adsorption of Gases by Solids," 1932.

(2) J. E. Lennard-Jones, *Trans. Faraday Soc.*, **28**, 333 (1928).

(3) T. Alty, *Phil. Mag.*, **15**, 1035 (1933).

(4) R. M. Barrer, *J. Chem. Soc.*, 376 (1934).