[CONTRIBUTION FROM THE DEPARTMENT OF METALLURGY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Vapor Pressure of Water above Saturated Lithium Chloride Solution

BY NEVZAT A. GOKCEN

The vapor pressure of water above saturated lithium chloride solution in the range of 23.90 to 54.84°, was determined with an average accuracy of ±0.3% by the gas current method using hydrogen. The solid phase is $LiCl \cdot H_2O$ throughout the range covered.

Introduction

Reported values by different observers[1,2] on the vapor pressure of water above saturated lithium chloride solution are not in satisfactory agreement, and in consequence new measurements have been carried out by the gas current method using hydrogen. Reliable values were obtained by this method in the range of pressures between 2 and 17 mm.

Accurate information was needed for controlled mixtures of very low water vapor content with hydrogen.[3,4] At higher levels of moisture such gas mixtures can be obtained by bubbling hydrogen through pure water at controlled temperatures. The inconvenience of obtaining thermostatic temperatures in the range of −15 to +18° prompted the use of saturated lithium chloride solution at higher temperatures and required a redetermination of its vapor pressure curve.

Experimental

A brief summary of the procedure is as follows: (a) Hydrogen was saturated by bubbling through a system consisting of four towers, each of which contained the solution of lithium chloride and some excess crystals of this salt. The impurities in the lithium chloride of C.P. grade were Ca 0.01, ClO_3 0.02, other alkalies 0.5, and SO_4 0.01. The towers were designed and filled with decreasing levels in order to minimize the errors due to the hydrostatic effect. The performance of this system was tested by using distilled water as a standard.

(b) Analysis of the saturated hydrogen for its water vapor content was made by using two U tubes in series containing fresh P_2O_5 and weighing the amount of absorbed water. Nearly all the moisture was absorbed by the first tube. The accuracy in these determinations required a minimum volume of 6 l. of hydrogen which was bubbled through at a rate of 100 ml. per minute. The volume of hydrogen and its pressure after being saturated were accurately measured. The temperature of thermostat was kept constant within ±0.02°.

The calculation of the equilibrium vapor pressure was made by assuming that the mixture $H_2 + H_2O$ behaves as an ideal gas mixture. The ideality correction for the vapor pressure ranges investigated here is below 0.07%.[5]

Results

The results presented in Table I and represented graphically in Fig. 1 were reproducible within ±0.02 mm. of mercury or better. Throughout the range covered,[6] the solid phase is $LiCl \cdot H_2O$.[7] The agreement between this and the previous results is not satisfactory. It should be emphasized that the reproducibility among the results of the previous investigators[1,2] was poor. The single determination of Lannung[8] agrees well with the extrapolated values of the present work, but the composition of the solid phase in his experiments was uncertain.

TABLE I

VAPOR PRESSURE OF SATURATED LITHIUM CHLORIDE SOLUTION

This investigation			Other investigations		
Temp., °C.		Press., mm.	Temp., °C.	Press., mm.	
23.90		2.64	18.00	1.71	Reference 8
23.90		2.63	20.0	2.2	Reference 1
23.90		2.63	30.0	3.6	Reference 1
23.90	Av.	2.63	35.0	4.6	
29.90		2.91	40.5	6.2	Reference 1
29.90		2.94	45.0	7.4	Reference 1
29.90	Av.	2.93	50.0	10.2	
34.90		5.31	51.0	10.0	Reference 1
34.90		5.32	55.0	12.4	Reference 1
34.90		5.32	58.5	13.8	Reference 1
34.90	Av.	5.32	60.45	14.9	Reference 2
39.90		7.28	61.35	15.9	Reference 2
39.90		7.26	70.00	26.6	Reference 2
39.90		7.25	70.45	26.2	Reference 2
39.90	Av.	7.26	80.15	37.9	Reference 2
44.90		9.83	85.15	46.0	Reference 2
44.90		9.83			
44.90		9.81			
44.90	Av.	9.82			
54.84		16.69			
54.84		16.71			
54.84	Av.	16.70			

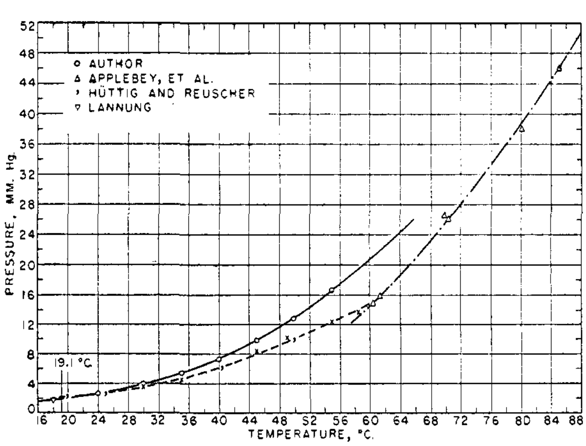

Fig. 1.—Vapor pressure of saturated lithium chloride solution at various temperatures.

A plot of log P *versus* $1/T$ yields a line of slight

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[1] F. H. Huttig and F. Reuscher, *Z. anorg. Chem.*, **137**, 155 (1924).

[2] M. P. Applebey, F. H. Crawford and K. Gordon, *J. Chem. Soc.*, 1665 (1934).

[3] M. N. Dastur and J. Chipman, *Metals Transactions*, **185**, 441 (1950).

[4] N. A. Gokcen, Sc.D. Thesis, Massachusetts Institute of Technology, 1951.

[5] J. H. Keenan and F. G. Keyes, "Thermodynamic Properties of Steam," John Wiley and Sons, Inc., New York, N. Y., 1950.

[6] M. P. Appelbey and R. P. Cook, *J. Chem. Soc.*, 547 (1938).

[7] The transformation of $LiCl + H_2O = LiCl \cdot H_2O$ occurs at 93.55° and that of $LiCl \cdot H_2O + H_2O = LiCl \cdot 2H_2O$ at 19.1° with a probable accuracy of ±0.05° as determined by the measurements of Appelbey and co-workers.[6]

[8] A. Lannung, *Z. physik. Chem.*, **A170**, 134 (1934).

curvature owing to an appreciable variation in the solubility. The effect of solubility on the curvature of such a plot is discussed elsewhere in sufficient detail.[9]

[9] A. E. Hirschler, THIS JOURNAL, 58, 2472 (1936).

CAMBRIDGE, MASS. RECEIVED FEBRUARY 21, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

A Study of Effect of Impingement-Particle Velocity in Radiolysis of Some Aromatic Hydrocarbons[1,2,3]

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Total-gas 100 ev. yields (*i.e.*, G values) in radiolysis of toluene, ethylbenzene, *i*-propylbenzene and *t*-butylbenzene in the Oak Ridge nuclear reactor are, respectively, 0.18, 0.27, 0.27 and 0.22, all values being slightly higher (10–30%) than yields obtained in electron bombardment radiolysis. At the same time, in every case studied, the ratio $G(H_2)/G(CH_4)$ is increased in reactor exposures over the ratio in electron bombardment by a factor of approximately two, the factor increasing in the order of listing above.

If secondary reactions involving pairs of free radicals can compete with reactions involving single radicals, an essential difference may be expected between effects of slow and fast particle irradiation.[5] The work reported herein was intended to examine such a possibility by radiolysis in a pile of a group of aromatic compounds whose electron-induced radiolysis had already been studied. It was expected that differences obtained would be essentially qualitative because the energy imparted to a sample by radiation in a pile is attributable about half to neutrons and about half to gamma and X-rays. Only product gases volatile at −120° were determined.

Experimental

Preparations of Materials.—Toluene, Baker and Adamson quality, reagent, b.p. range 110–111° was fractionated in a column with 50 theoretical plates. A middle third of constant b.p. was retained; $n^{20}D$ 1.4965, $n^{20}D$ (lit.) 1.4969.

Ethylbenzene, Eastman Kodak White Label, b.p. range 134–136°, was fractionated in a column with 50 theoretical plates. A middle third of constant b.p. was retained; $n^{20}D$ 1.4956, $n^{20}D$ (lit.) 1.4959.

Samples of *i*-propylbenzene and *t*-butylbenzene employed in this work were from batches prepared for previous work on electron irradiation studies.[8]

Techniques for purification of all samples prior to exposure were identical with those previously described.[6]

Exposure Techniques.—The vessels for pile exposure were made entirely of quartz and were of cylindrical shape, internal diameter about 23 mm., internal length about 49 mm., and internal volume about 20 ml. At the end of the cylindrical vessel were attached a quartz break-off seal and a section of quartz tubing with a constricted region to which a graded seal was attached for the duration of the filling operation. Caution had to be exercised in freezing the liquids in the quartz vessels since supercooling resulted in cracking the quartz vessels. To prevent this, the liquids were first slowly frozen by an ethyl bromide mush (−120°); they could then be cooled with liquid nitrogen.

The cells were less than half-filled, with sample volumes ranging from 6 to 9 ml. The samples were exposed for periods of 8 and 16 hours in a central region of the graphite pile at the Oak Ridge National Laboratory. The hole in which the samples were exposed was cooled by a stream of running water maintained at a temperature of 15–20°; the samples were consequently at somewhat higher temperature. (In the electron irradiation studies with which comparison is made, temperature was maintained at about 20–25° by cooling water.)

The four substances herein reported were exposed simultaneously to insure correct relative G values. Gas yields were found to be a linear function of exposure.

The following figures for energy dissipation per gram of certain atoms are used in calculation of energy dissipation in their compounds.[7]

Element	Cal. g.$^{-1}$ sec.$^{-1}$
C	0.00046
H	.0075

Analyses.—Analyses of gaseous products for H_2, CH_4 and C_2 fractions were performed in a Saunders–Taylor semimicro gas analysis apparatus[8] essentially as described by Hentz and Burton.[9] The mass spectrometer was used for positive identification of methane and for analysis of the C_2 fraction.

Results and Discussion

The chemical effects of electron irradiation of toluene, ethylbenzene, *i*-propylbenzene and *t*-butylbenzene have been previously reported from these laboratories.[6,9] These same compounds were selected for a study of chemical effects of pile irradiation to determine effect of impingent particle velocity. Table I summarizes the results of this investigation. Table II compares the 100 ev. yields (G values) calculable from Table I with results previously obtained on irradiation with 1.5 and 1.8 Mv. electrons.[6,9] The discrepancy between G values of hydrogen for pile and electron irradiation is small.

TABLE I

SUMMARY OF PILE IRRADIATION DATA

	% H_2	% CH_4	% C_2 gas	G_t[a]
Toluene	87.6	3.4	9.0	0.18
Ethylbenzene	83.2	8.6	8.2	.27
i-Propylbenzene	77.5	18.5	4.0	.27
t-Butylbenzene	72.1	20.6	8.3	.22

[a] The number of molecules of gas produced volatile at −120° per 100 ev. absorbed.

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[1] Contribution from the Radiation Chemistry Project operated by the University of Notre Dame under Atomic Energy Commission contract AT(11-1)-38.

[2] The nuclear reactor exposures described herein were performed in the graphite reactor of the Oak Ridge National Laboratory.

[3] This paper is an abstract from a thesis submitted by Thomas J. Sworski to the Department of Chemistry of the University of Notre Dame in partial fulfillment of requirements for the degree of Doctor of Philosophy.

[4] Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

[5] *Cf.* M. Burton, *J. Phys. Colloid Chem.*, 51, 611 (1947).

[6] T. J. Sworski, R. R. Hentz and M. Burton, THIS JOURNAL, 73, 1998 (1951).

[7] D. M. Richardson, ORNL-129, The Calorimetric Measurement of Radiation Energy Dissipated by Various Materials in the Oak Ridge Pile.

[8] K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, 9, 616 (1941).

[9] R. R. Hentz and M. Burton, THIS JOURNAL, 73, 532 (1951).