TABLE III

Element	Quantum numbers {n...1	2		3			4				5				6				7	Highest
	{l....s	s	p	s	p	d	s	p	d	f	s	p	d	f	s	p	d	f	s	valency
91 Et	2	2	6	2	6	10	2	6	10		2	6	10		2	6	3		2	5
92 U	2	2	6	2	6	10	2	6	10		2	6	10	1	2	6	4		1	6
93	2	2	6	2	6	10	2	6	10		2	6	10	2 (1)	2	6	4 (5)		1	5 (6)
94	2	2	6	2	6	10	2	6	10		2	6	10	3	2	6	4		1	5
95	2	2	6	2	6	10	2	6	10		2	6	10	4	2	6	4		1	5
etc.																				

ment will be bound in a lower quantum level and not be available as a valence electron.

We may assume that the filling of this lower quantum level has begun already in uranium; in this case the electron distribution would be given by Table III, according to the most reliable present knowledge.

Uranium would then correspond to cerium in the first group of rare earths and elements 93 and 94, also 95 and 96, etc., would all have properties very similar to element 91, just as the chemical properties of Pr, Nd, Sm, etc., are practically identical with La, and elements 93, and 94 in that case, would *not have* the properties of ekarhenium and ekaosmium.

It might also be that the filling up of the n_5 quantum level will begin at element 93, or 94, or even later; in the first case element 93 will be similar to uranium, just as Ce resembles La, and only in special cases resemble rhenium (like Ce ⟶ Zr).

A definite decision as to the real nature of these elements could be made after calculating the energy levels of the trans-uranium elements. For this purpose the energy levels of three last elements in the periodic table (Th, Et and U) should be known exactly. Unfortunately, the optical spectra of these elements have so far not yet been elucidated, due to their extreme complexity. We hope that the importance of these data for nuclear research may stimulate work in this direction.

Summary

The chemical properties of elements 93 and 94 are deduced (1) according to the periodic law and (2) according to the Bohr theory.

CHICAGO, ILL. RECEIVED DECEMBER 11, 1934

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

The Vapor Pressure of Binary Solutions of Ethyl Alcohol and Cyclohexane at 25°

BY E. ROGER WASHBURN AND BENJAMIN H. HANDORF

A previous investigation[1] indicated that solutions of ethyl alcohol in cyclohexane deviated widely from ideality. A further study of this system has been concerned with vapor pressure relationships. The total pressures and the partial vapor pressures of the components of solutions of ethyl alcohol and cyclohexane throughout the concentration range have been measured at 25°.

Materials

The ethyl alcohol and cyclohexane used in this investigation were obtained from the same sources and were purified by the same procedures as described in the previous investigation.[1] The resulting products were of the same quality as those there described. Merck C. P. silver nitrate was dissolved in redistilled water in preparing the solutions for the silver coulometer.

Method and Apparatus

Pearce and Snow's modification[2] of the air-bubbling method for measuring vapor pressure was adapted for this study. A mixture of hydrogen and oxygen, generated by the electrolysis of a 25% solution of sodium hydroxide contained in six large bottles, was saturated with the vapors of the mixtures under investigation. The amount of gas generated was calculated from the weight of silver deposited in a silver coulometer connected in series with the generators. The gas was dried with sulfuric acid before it entered the series of four bubblers, each of which contained from 8 to 10 cc. of the mixture being studied. The bubblers were connected in series by ground glass joints fitted with mercury seals. They were immersed in a constant temperature water-bath at the desired temperature. The vapors of the organic liquids were condensed out of the gas mixture in a tube immersed in a mixture of solid carbon dioxide and ether. Several determinations were made on alcohol rich mixtures and on pure alcohol using liquid air as the condensing medium.

The results thus obtained checked very closely those secured using solid carbon dioxide and ether and showed the latter condensing medium to be practically as efficient as the former.

The condensing tube was stoppered and weighed on an

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[1] Vold and Washburn, THIS JOURNAL, **54**, 4217 (1932).

[2] Pearce and Snow, *J. Phys. Chem.*, **31**, 231 (1927).

analytical balance in determining the weight of the condensed vapors. The refractive index of this liquid was determined by means of an immersion refractometer, and the composition was then read from a refractive index–composition curve which had been experimentally determined.

Calculation of Results

The number of moles of hydrogen and oxygen from the generators in one experiment was obtained by dividing the weight of silver deposited in the coulometer by 23.9733 which is one-ninth of twice the equivalent weight of silver. (Each two equivalents of silver deposited indicated that in the six generators six moles of hydrogen and three moles of oxygen had been liberated.)

The number of moles of alcohol and of cyclohexane was calculated from the composition and weight of the condensed vapors and the molecular weights of the components.

The number of moles of vapor thus obtained multiplied by the atmospheric pressure and divided by the total number of moles of vapor and hydrogen and oxygen gave the total vapor pressure of the mixture.

The partial vapor pressure of one of the components was obtained by multiplying the mole fraction of that component in the vapor by the total vapor pressure.

Results and Discussion

The experimental data obtained at 25° are recorded in Table I and the various quantities calculated from the data are recorded in Table II. Each recorded value is the average of three independent determinations on the same solution. The activity coefficients for alcohol and cyclohexane are recorded in columns 5 and 6, respectively, of Table II. They were calculated by means of the equation $f = p/p^\circ N$ where f is the activity coefficient, p is the partial vapor pressure of the component above the solution and p° is the vapor pressure of the pure component, N is the mole fraction of the component in the solution.

TABLE I

EXPERIMENTAL DATA AT 25°

M. F. C. in liquid	Refractive index. Liquid	Vapor	Silver, g.	Vapor, g.	Pressure, mm.
0.0000	1.35935		3.4788	0.5727	725.19
.1008	1.36867	1.39916	2.5933	1.2316	735.09
.2052	1.37766	1.40524	2.5094	1.5256	729.54
.2902	1.38412	1.40611	2.5029	1.6390	729.53
.4059	1.39216	1.40623	2.5237	1.7309	731.31
.5017	1.39836	1.40666	2.2454	1.5793	726.98
.5984	1.40342	1.40695	2.5311	1.7565	733.72
.7013	1.40890	1.40723	2.5214	1.7629	732.59
.7950	1.41356	1.40748	2.3197	1.6277	734.79
.8970	1.41855	1.40830	1.9216	1.3340	731.05
1.0000	1.42338		1.9477	1.0347	739.84

TABLE II

PARTIAL AND TOTAL VAPOR PRESSURE RELATIONSHIPS AT 25°

Mol. fraction cyclohexane Liquid	Vapor	Vapor pressure, mm. Ethyl alcohol	Cyclohexane	Activity coefficient f_a	f_c
0.0000	0.0000	57.3		1.000	
.1008	.5204	52.0	56.4	1.009	5.746
.2052	.6304	46.4	79.2	1.020	3.967
.2902	.6468	46.8	85.8	1.153	3.037
.4059	.6490	48.4	89.5	1.423	2.266
.5017	.6576	47.7	91.7	1.673	1.878
.5984	.6632	46.8	92.1	2.034	1.582
.7013	.6687	46.1	93.0	2.695	1.363
.7950	.6732	45.9	94.6	3.913	1.222
.8970	.6895	42.5	94.3	7.205	1.081
1.0000	1.0000		97.3		1.000

The experimentally determined values for the vapor pressure of pure ethyl alcohol at 25° were about 3% low as compared with the values listed in the literature.[3]

Corresponding values for cyclohexane checked the literature[4] values within 0.5%.

Several attempts were made to improve the experimentally determined value for the vapor pressure of alcohol by substituting liquid air and sulfuric acid, respectively, for the carbon dioxide–ether mixture as the condensing medium. In each case the values were practically the same and were about 3% below the literature values. Because of this fact the vapor pressure of the ethyl alcohol at 25° was determined by the Smith–Menzies isoteniscope method. The values obtained checked the literature value very well, and indicated that the above error was not due to impurities in the alcohol.

The system ethyl alcohol–cyclohexane has been found to exhibit very large positive deviations from Raoult's law. The deviations of the calculated values for the activity coefficients from one measure quantitatively the deviations of the solutions from Raoult's law. The wide deviations from ideal behavior exhibited by the system ethyl alcohol–cyclohexane occurred because of the great difference in polarity and internal pressure of the two components. One of the most direct evidences of the polarity of a liquid is the magnitude of its dielectric constant. At 20° the dielectric constant of cyclohexane is 2.05, while for ethyl alcohol it is 25.7. Relative internal pressures were calculated using boiling point and molecular volume data by means of the equation: internal pressure = $(5200 + 30\ t_b)/V$ at 20°, where t_b is the boiling point of the liquid and V is

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(3) "Int. Crit. Tables," Vol. III, p. 217.

(4) Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

the molecular volume of the liquid. The values secured were as follows: cyclohexane, 70.6; ethyl alcohol, 129.4.

It is apparent from a comparison of the dielectric constants of the liquids as well as of the internal pressures that in pure liquid alcohol the attractive forces between the molecules are much greater than in pure cyclohexane. In dilute solutions of ethyl alcohol in cyclohexane the ethyl alcohol molecules are widely separated by the interspersed cyclohexane molecules. As a result the attractive forces between the ethyl alcohol molecules are negligible as compared with that in pure ethyl alcohol and the relative escaping tendency of the ethyl alcohol is much greater than in pure ethyl alcohol. As a result the vapor pressure of ethyl alcohol in such solutions exhibits wide deviations from Raoult's law. Since the ethyl alcohol molecules are too far apart to attract each other appreciably, they exert little squeezing out effect on the cyclohexane molecules and consequently the cyclohexane vapor pressure deviates but slightly from ideal behavior in solutions dilute in ethyl alcohol. In solutions concentrated in ethyl alcohol, the ethyl alcohol molecules are but slightly separated by the cyclohexane molecules. The separation, however, is not sufficient to alter appreciably the attractive forces between the alcohol molecules. Therefore, the effect of the added cyclohexane is merely that of reducing the number of molecules per unit volume and the result is only a slight deviation from Raoult's law. However, in such solutions cyclohexane exhibits large deviations from Raoult's law because of the squeezing out effect produced by the ethyl alcohol molecules, whose attraction for each other is much greater than the attraction of the cyclohexane molecules for each other or for the alcohol molecules. At intermediate concentrations the deviations of each component from ideal behavior are intermediate between their respective deviations in dilute and concentrated solutions, as would be expected on the basis of the explanation given.

Summary

1. A modification of the dynamic method for measuring vapor pressures devised by Pearce and Snow has been adapted to the determination of the total vapor pressure, and the partial vapor pressures of the components of binary solutions of ethyl alcohol and cyclohexane, ranging in concentration from pure alcohol to pure cyclohexane, at 25°.

2. The data have been used to calculate the activity coefficients, which indicate the deviations from Raoult's law.

3. Deviations from ideal behavior have been discussed and explained on the basis of the difference in polarity and internal pressure of the two components.

LINCOLN, NEBRASKA RECEIVED DECEMBER 24, 1934

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 448]

The Photo-oxidation of Liquid Carbon Tetrachloride

BY ERNEST H. LYONS, JR., AND ROSCOE G. DICKINSON

When liquid carbon tetrachloride is illuminated in an open quartz vessel by a quartz mercury arc, reaction occurs; the main reaction has been supposed[1] to be given by the equation $2CCl_4 \longrightarrow C_2Cl_6 + Cl_2$. The use of carbon tetrachloride as an actinometric substance for use in therapeutic work has been considered.[2]

We have found, in preliminary experiments, that carbon tetrachloride irradiated in the above manner develops a strong odor of phosgene; and if the liquid is then shaken with water, an acid solution results which oxidizes potassium iodide. Evidently, when carbon tetrachloride is irradiated in the presence of oxygen, some oxidation occurs; moreover, since the total amount of reaction is ordinarily not large, further complication may arise from the presence of traces of water. Consequently we have undertaken to exclude water and to determine the effect of ultraviolet light on carbon tetrachloride first in the absence of oxygen, and second, in its presence.

The photochemical procedure we have used has

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[1] See, for example, Benrath and Hertel, *Z. wiss. Phot.*, **23**, 30 (1924); Morton, "Radiation in Chemistry," D. Van Nostrand Co., New York, 1928, pp. 55, 119.

[2] Mackenzie and King, "Practical Ultraviolet Therapy," Benn, 1926; Hymas. *Quart. J. Pharm.*, **2**, 281 (1929).