ent acidities. The mobility varied between 13.6 × 10^{-5} cm.^{2} sec.$^{-1}$ volt^{-1} towards the cathode at P_H = 3.40, and 7.9 × 10^{-5} cm.^{2} sec.$^{-1}$ volt^{-1} towards the anode at P_H = 5.75, all at t = 13.5°. The values obtained show some departure from those found by Svedberg and Scott using fluorescence to make the protein visible. It is shown that the absorption method is to be considered as more reliable.

Further work by this method with an improved apparatus is in progress.

UPSALA, SWEDEN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

OXIDATION POTENTIALS IN LIQUID AMMONIA INVOLVING QUATERNARY AMMONIUM RADICALS AND ALKALI METALS

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This research was undertaken primarily to compare the oxidation potentials of systems of the type $NR_4 - \ominus \rightleftarrows NR_4^+$, where the R's are various alkyl groups. It appeared that such a potential series would be of value in the systematic study of alkyl groups and of quinquivalent nitrogen alike. Later we included the alkali metals, the better to correlate them with the quaternary radicals.

An examination of the literature indicated the difficulties of such an undertaking. Crotogino[1] electrolyzed water solutions of mono-, di- and trimethyl- and triethylammonium oxalates on a mercury cathode, and compared the positions of the breaks on the polarization curves. McCoy and Moore[2] prepared mono- and tetramethylammonium amalgams by electrolysis of solutions in absolute alcohol; the e.m.f. of their products measured against an aqueous calomel electrode varied with time. Podrouzek[3] electrolyzed water solutions of ammonium, tetramethyl and tetraethyl salts upon dropping mercury cathodes, obtaining results not very similar to those of Crotogino. Examination of the above-mentioned papers, and of papers on ammonium amalgams, revealed many objections to the use of mercury and to working temperatures above its freezing point. On the other hand, the literature concerning the preparation of quaternary ammonium radicals in liquid ammonia offered a better prospect of arranging the former in a potential series.

Palmaer[4] noted blue streaks near a cathode in a solution of tetramethylammonium chloride in liquid ammonia. Eleven years later Kraus[5] observed the same effect with tetramethyl and also with tetrapropyl salts.

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[1] Crotogino, *Z. Elektrochem.*, **7**, 648 (1901).

[2] McCoy and Moore, THIS JOURNAL, **33**, 273 (1911).

[3] Podrouzek, *Rec. trav. chim.*, **44**, 591 (1925).

[4] Palmaer, *Z. Elektrochem.*, **8**, 729 (1902).

[5] Kraus, THIS JOURNAL, **35**, 1732 (1913).

Schlubach[6] and his associates have worked extensively upon quaternary ammonium radicals in liquid ammonia, electrolyzing chlorides or iodides at —70° in a vacuum. The products reduced iodine, sulfur, 2,6-dimethylpyrone, oxygen and acetylene. The blue radicals, on standing, yielded a colorless solution giving similar reactions. Substitution of hydrogen or of aryl groups increased instability, but Schlubach[6c] and Ballauf reported a colorless solution of free ammonium produced by the action of potassium on ammonium chloride in liquid ammonia. In addition, Schlubach and Miedel[6e] obtained tetra-ethylphosphonium, -arsonium and triethylsulfonium radicals.

Gibson and Argo[7] have investigated the spectra of alkali metals in liquid ammonia, and have shown that there is strong absorption in the red, as Schlubach and Ballauf also noted with quaternary ammonium radicals. The highly important work of Kraus and his associates upon alkali metals in liquid ammonia is discussed below.

Materials.—Tetramethyl- and tetra-ethylammonium bromides from the Eastman Kodak Company, and triethyl-*n*-butylammonium bromide kindly furnished by Professor C. S. Marvel of the University of Illinois were treated with silver oxide and the product was neutralized with hydriodic acid. In general, chlorides and bromides proved less satisfactory than iodides. Tetrapropylammonium iodide was purchased from Kahlbaum. We synthesized tetrabutyl-, methyltributyl-, trimethylbutyl-, tripropylbutyl- and ethyltributylammonium iodides from the proper tertiary amines and alkyl iodides. Diethyldibutylammonium iodide was prepared for us from dibutylamine and ethyl iodide by Mr. W. F. Hester of this Laboratory under the direction of Professor E. P. Kohler. We are very grateful for their kind coöperation. Two recrystallizations from water, or alcohol or acetone with centrifugal drainage yielded products cream-colored in most cases, which were dried over potassium hydroxide. Apparently diethyldibutyl, tripropylbutyl, methyltributyl and ethyltributyl salts have not hitherto been prepared. Like Hofmann and Reimer[8] we could not isolate a tetra-*iso*butyl compound. All products were analyzed by the Volhard method and had the proper iodine content within 0.5%.

Apparatus and Procedure.—Fig. 1 shows our cell in its final form. It made possible the preparation of solutions of quaternary iodides in liquid ammonia, electrolysis at —78° with rigorous exclusion of oxygen and moisture, measurement against a constant reference electrode of oxidation potentials of the systems $NR_4 - \ominus \rightleftarrows NR_4^+$, and determination of concentrations actually prevailing at the moment of such measurements.

The lower compartment E, shut off by the ground joint F, contained an electrode of silver foil M silver-plated and gently ignited, and was filled with liquid ammonia, distilled from sodium and saturated with silver nitrate carefully fused to eliminate moisture. Above the ground joint were two alundum cups I, surrounded by platinum gauze cathodes J. The cups contained the anodes K, connected in parallel, and some

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[6] Schlubach and others, (a) *Ber.*, **53**, 1689 (1920); (b) **54**, 1689, (c) 2811, (d) 2825 (1921), (e) **56**, 1889, (f) 1892 (1923).

[7] Gibson and Argo, THIS JOURNAL, **40**, 1327 (1918).

[8] Hofmann and Reimer, *Ber.*, **3**, 757 (1870).

quaternary salt. Three pipets, N, contained carefully dried silver iodide rather than silver nitrate, as nitrates, we proved, oxidize the blue radicals. The platinum electrode L served for potential measurements only, but the gauze electrode showed the same e.m.f. a few seconds after cessation of electrolysis. If, however, the gauze electrode was connected alternately to dynamo and potentiometer by a rapidly revolving commutator, abnormally large and variable e.m.f. resulted. The stopper A of the cell was accurately ground; it bore the chimneys H and the inner tube C through which the various wires and tubes emerged.

Before being assembled, the cell was dried at 130° for several hours. Silver nitrate was dropped into E, and the joints were closed with sealing wax. The cell was heated for several hours more in a vertical tubular oven; meanwhile, there was passed through it nitrogen prepared by the Wanklyn process and purified with boiled sulfuric acid, properly aerated pentoxide and hot copper. After introduction of the quaternary iodide the cell was swept out for four hours more and then immersed in liquid ammonia in a Dewar vessel. By means of liquid nitrogen this bath could be maintained at the triple point of ammonia, —78°. Commercial liquid ammonia was treated with an excess of sodium in a glass-stoppered distilling flask, and the gas distilled through a trap into the cell. The lower compartment was entirely filled, also the upper one and the cups to the level I, but not the pipets. Electrolysis followed, using 40 to 25 volts and 0.05 to 0.2 ampere, varying with the solubilities of the several iodides. The e.m.f. of the cell $Ag^+ \mid AgNO_3 \mid NR_4\ NR_4I \mid Pt^-$ was measured with frequent agitation on an accurate Wolff potentiometer kindly lent by Professor Grinnell Jones. Readings of e.m.f. were referred to a standard Eppley cell. No interruption in the nitrogen current was

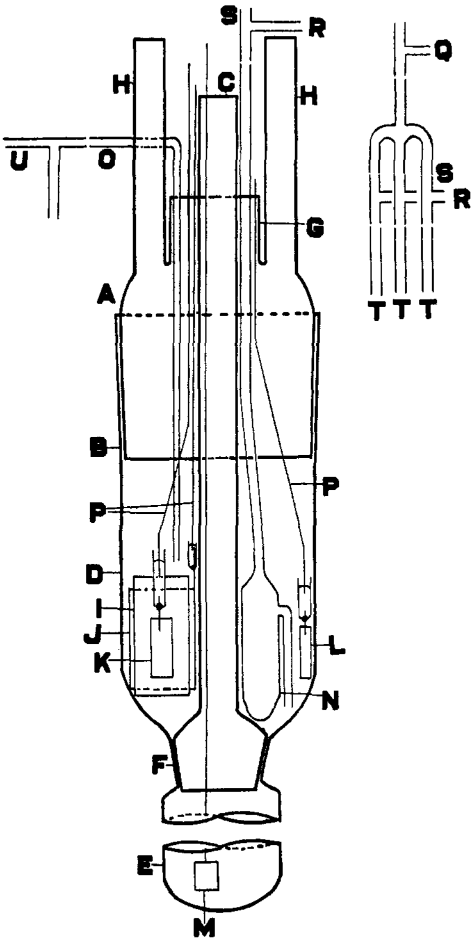

Fig. 1.—Cell for measurement of oxidation potentials.

tolerated. Much time was expended before our precautions were sufficient to prepare solutions giving readings constant within a few millivolts. These free radicals, we found, are vastly harder to handle than the alkali metals.

After the first measurement of e.m.f. one pipet containing silver iodide was filled with the blue solution by increasing the nitrogen pressure outside of it, and metallic silver was at once precipitated. Electrolysis, potential measurement and sampling were then twice repeated. Next, the cell was taken apart, and the position of the meniscus on each pipet was marked. After evaporation of the ammonia, the top of each pipet was cut off and the contents were transferred to a filter, the original volume of the sample being previously determined. After all soluble iodide had been washed out, the metallic silver was dissolved in dil. nitric acid and titrated according to Volhard, two end-points being secured in each case. As an excess of

TABLE I

CONCENTRATIONS AND ELECTROMOTIVE FORCES

Material	$[NH_4]$ $\times 10^4$	$[NR_4I]$ $\times 10^4$	E.m.f.	Material	$[NR_4]$ $\times 10^4$	$[NR_4I]$ $\times 10^4$	E.m.f.
$N(CH_3)_4I$	26	23	2.592	$N(CH_3)_3C_4H_9I$	32	1005	2.585
	26		2.594		41		2.594
	46		2.592		54		2.599
$N(C_2H_5)_4I$	29	105	2.594	$N(C_2H_5)_3C_4H_9I$	57	303	2.585
	36		2.597		55		2.596
	46		2.599		45		2.600
					63		2.597
					71		2.609
					51		2.612
$N(C_3H_7)_4I$	62	81	2.580	$N(C_3H_7)_3C_4H_9I$	12	46	2.580
	54		2.595		12		2.566
	41		2.590		23		2.581
	12		2.604		26		2.604
	42		2.612				
	32		2.603				
	09		2.605				
	16		2.613				
	27		2.613				
$N(C_4H_9)_4I$	16	39	2.558	$NCH_3(C_4H_9)_3I$	13	813	2.589
	24		2.579		14		2.596
	26		2.579		12		2.600
	38		2.592		13		2.594
	79		2.596		22		2.597
	24		2.593				
	45		2.599				
$N(C_2H_5)_2(C_4H_9)_2I$	43	330	2.602	$NC_2H_5(C_4H_9)_3I$	58	259	2.582
	12		2.607		40		2.591
	24		2.610		47		2.596
	16		2.607				
	15		2.608				
	32		2.614				

solid salt was always present after electrolysis, and as the cell was frequently agitated, its constant concentration was found by preparing new saturated solutions at —78° in Pyrex test-tubes, which were sampled as described above, and analyzed either by weighing the residue or by the Volhard method. The solubilities at —78° in moles per liter are given below in Table II with a probable error of 10%.

Table I gives actual measurements of e.m.f. and of concentrations in moles per liter in cells of the type $Ag^+ \mid AgNO_3$ satd. $\mid NR_4\ NR_4I \mid Pt^-$. $[NR_4]$ is here tabulated without allowance for dissociation into ion and electron, a point which is discussed below. All measurements in our final series are included.

Table II includes cells of the type $Pt \mid M + MINR_4 + NR_4I \mid Pt$ with the alkali metal M and its salt MI in Compartment E, also a third type of cell with two alkali metals.

TABLE II

QUARTERNARY RADICALS AND ALKALI METALS

$[N(C_2H_5)_2(C_4H_9)_2]$	$[N(C_2H_5)_2(C_4H_9)_2I]$	$[Na^+]$	$[NaI]$	Positive pole	E.m.f.
0.002	0.033	0.008	0.01	NR_4	0.006
.002	.033	1.0	.01	NR_4	.009
$[N(C_3H_7)_4]$	$[N(C_3H_7)_4I]$	$[K^+]$	$[KI]$	Positive pole	E.m.f.
0.003	0.0083	0.014	0.052	NR_4	0.005
.004	.0083	1.2	.052	NR_4	.018
.004	.0083	1.2	1.04	NR_4	.015
$[Li^+]$	$[LiI]$	$[Na^+]$	$[NaI]$	Positive pole	E.m.f.
0.02	0.002	0.08	0.002	Na	0.023
.10	.002	.08	.002	Na	.003
.10	.006	.08	.002	Na	.001

We now desired to reduce the above data to a consistent concentration basis. Because of limited concentration range of the radicals and errors in measuring e.m.f., the average value of $\Delta E/\Delta \log [NR_4]$ is a small negative quantity. Table II indicates that $\Delta E/\Delta \log [M]$ and $-\Delta E/\Delta \log [MI]$ are both very small. We also investigated $\Delta E/\Delta \log [NR_4I]$ by dropping into cells of the type first described additional quantities of quaternary iodides thoroughly dried and freed from absorbed air by pure nitrogen. The order of operations was electrolysis of an unsaturated solution sample, addition of salt to saturation, electrolysis, sample; addition of more salt, electrolysis, sample (see Table III).

TABLE III

CONCENTRATION EFFECTS

$[N(C_2H_5)_2\text{-}(C_4H_9)_2]$	$[N(C_2H_5)_2\text{-}(C_4H_9)_2I]$	E.m.f.	$[N(C_2H_5)\text{-}(C_4H_9)_3]$	$[N(C_2H_5)\text{-}(C_4H_9)_3I]$	E.m.f.
0.0010	0.015	2.593	0.0022	0.020	2.604
.0010	.032	2.589	.0022	.059	2.595
.0005	.032	2.597	.0011	.059	2.605

The effect of doubling or trebling the concentration of an iodide is seen to be small. Even the sign of the correction is in doubt.

All the data, therefore, showed that the equation $E_0 = E + RT\,ln([NR_4]/[NR_4^+])$ was inadequate, at least, if concentrations were calculated from analytical data. Indeed, values of E_0 thus calculated for the several radicals stood in the same order as the solubilities of the corresponding quaternary iodides. Kraus's[9] theory of alkali metals in liquid ammonia, when extended to our radicals, suggested a more rational method of interpolation. Kraus holds that in such solutions (dilute) $Na + nNH_3 \rightleftarrows Na^+ + \ominus.nNH_3$, where the negative carrier is a solvated electron. He assumes that the electrons do no work at phase boundaries, and that potentials of *dilute* sodium concentration cells in liquid ammonia are determined solely by the junction potential, $E = (2nRT/F).ln[Na^+]_1/[Na^+]_2$. From his data we built up a curve from which the e.m.f. of any cell involving two sodium concentrations could be interpolated. Assuming analogous relations in concentration cells involving quaternary ammonium radicals, it appeared that the correction for $\Delta E/\Delta \log [NR_4]$, which we were unable to evaluate, should not exceed a few millivolts. The equilibrium $NR_4 - \ominus \rightleftarrows NR_4^+$ is peculiar in that any change in either concentration will tend to change the other in the same sense without transfer of electrons between solution and electrode. In consequence, the ratio $[NR_4]/[NR_4^+]$ is hard to vary through wide limits. As Kraus's sodium cells also were in a high degree reversible, the analogy thus renders void an argument against the reversibility of our cells, and also supplies one in its favor.

We have calculated very roughly the changes in junction potentials of our cells corresponding to a change in quaternary iodide concentration to 0.005 *M* in each case. We used the equation of Henderson, and assumed for lack of adequate data (1) that all mobilities are in the same ratio in water and in liquid ammonia at —35° or —78°; (2) that the "degree of dissociation" is invariably one-half; (3) that the total correction is half the sum of those calculated separately for variations in concentration of free radical and of quaternary iodide. The last column of Table IV embodies

TABLE IV

SOLUBILITIES AND CORRECTED E.M.F.

Radical	Soly. NR_4I at −78°	E.m.f. obs. av.	E.m.f. 0.005*M*	Radical	Soly. NR_4I at −78°	E.m.f. obs. av.	E.m.f. 0.005*M*
$N(CH_3)_4$	0.0023	2.593	2.585	$N(CH_3)_3C_4H_9$	0.10	2.592	2.590
$N(C_2H_5)_4$	.010	2.597	2.590	$N(C_2H_5)_3C_4H_9$	.031	2.600	2.595
$N(C_3H_7)_4$	.0083	2.602	2.596	$N(C_3H_7)_3C_4H_9$	.0063	2.583	2.578
$N(C_4H_9)_4$	.0039	2.585	2.578	$N(C_4H_9)_3CH_3$	.081	2.596	2.595
				Metal	MI		
$N(C_2H_5)_2(C_4H_9)_2$	.033	2.597	2.595	Li	0.10	2.606	...
				Na	.008	2.603	2.594
$N(C_2H_5)(C_4H_9)_3$	.059	2.601	2.599	K	.05	2.601	...

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[9] Kraus, THIS JOURNAL, **30**, 1323 (1908); **36**, 864 (1914); **43**, 749 (1921).

these very dubious corrections, also averaged oxidation potentials against the saturated silver-silver nitrate electrode, and averaged solubilities.

When all the alkyl groups are alike, solubility of the iodide reaches a maximum with the ethyl compound and then falls off again. The increased solubility of the mixed salts is striking, but the cases studied are not numerous enough to permit of a comprehensive generalization.

The oxidation potentials of quaternary radicals and of alkali metals alike in equilibrium with electrons and ions all lie within 25 millivolts. Ruff and Geisel,[10] investigating the possibility of compound formation between sodium or potassium and (liquid) ammonia, incidentally state "in the case of solutions of these metals, measurable electromotive forces do not appear." They do not, however, specify what cells were measured. The variation of our averaged values for the several radicals is considerably greater than the probable error in any given average. This implies that the composition of the radical or metal exerts a small but definite specific influence upon its oxidation potential. We have thus far been unable to correlate this influence with composition, except to note that lithium, as Lewis and Keyes[11] found, appears to be the most electropositive. We prefer, therefore, to emphasize the approximate identity of oxidation potentials of quaternary radicals and of alkali metals, in the presence of their iodides, and the similarity between the fifth valence of nitrogen and that of the alkali metals, which is more strikingly demonstrated here than in any previous electrochemical research.

In addition to acknowledgments made above, we express our appreciation of a grant from the Milton Fund for Research, of liquid nitrogen furnished gratis by the Air Reduction and Sales Company, and of information about quaternary ammonium halides supplied by Professors E. P. Kohler and J. B. Conant.

Summary

An apparatus and a method have been devised for measurement of oxidation potentials of ten quaternary ammonium radicals in equilibrium with their ions and electrons on platinum against silver electrodes in saturated silver nitrate solution, all in liquid ammonia at its triple point. Comparisons with alkali metals were also made.

The concentrations of free radicals were determined in terms of silver, after reaction with silver iodide. The concentrations of the corresponding halides in saturated solution at —78° were also determined. The analytical errors were of the order of 10%.

The observed oxidation potentials of the radicals, also of lithium, sodium and potassium, all lie within 25 millivolts of one another. This

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[10] Ruff and Geisel, *Ber.*, **39**, 828 (1906).

[11] Lewis and Keyes, THIS JOURNAL, **35**, 340 (1913).

outcome upholds the analogy between the fifth valence of nitrogen and that of an alkali metal.

Data necessary to reduce all results to a comparable concentration basis are not available, but evidence is given that the corrections should be reckoned in millivolts rather than in centivolts.

The small differences in oxidation potentials, if conditioned by chemical composition, are not readily correlated with the latter.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE FREE ENERGY AND HEAT OF TRANSFER OF BARIUM IN ITS LIQUID AMALGAMS

BY PAUL A. ANDERSON

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The electromotive measurement of a series of liquid-amalgam concentration cells is capable of furnishing quite exact information regarding both the thermodynamic properties of the system and the specific state of the metal solute in its mercury solution. While this type of investigation has been extended to many of the commoner mercury-soluble metals, none of the amalgams of the alkaline earth group of metals has been subjected to satisfactorily exact study. Such a study of barium amalgam was the object of the work to be described.

The two general methods available for determination of the electromotive forces of concentration cells of the reactive alkali and alkaline earth amalgams involve, respectively, measurement in an aqueous electrolyte with the use of some form of renewable electrode, and measurement in some non-aqueous electrolyte that does not decompose the amalgam. Richards and Conant[1] applied the former method to sodium amalgam concentration cells and by the use of synchronously flowing drop electrodes obtained reproducible potentials down to a concentration of 0.17 atomic per cent. of sodium. Cady[2] applied the second method in his measurements of two cells of the type: Ba amalgam (C_1), BaI_2 in pyridine, Ba amalgam (C_2). Comparison of Cady's analyses with the solubility data of Kerp and Böttger[3] indicates that the amalgam of his concentrated electrode was highly supersaturated. His results, therefore, are of only qualitative significance.

Examination of Electrolytes

The problem involved in the measurement of the potentials of barium amalgam concentration cells was found to resolve itself largely into a

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[1] Richards and Conant, THIS JOURNAL, **44**, 601 (1922).

[2] Cady, *J. Phys. Chem.*, **2**, 551 (1898).

[3] Kerp and Böttger, *Z. anorg. Chem.*, **25**, 1 (1900).