(C) The potentials for glasses containing alkali oxides do not follow either pattern. They form a parabolic curve, shifted toward more negative potentials, which has a pronounced minimum for potassium oxide. This oxide is therefore the strongest base in our system, since a minimum in the e.m.f. means a maximum in the oxygen ion activity. This behavior can tentatively be explained on the basis of the random network theory by the interaction of two opposing effects: decreasing z/a^2 value, and increasing coördination requirements in the series from lithium to cesium. The increasing coördination (Warren, ref. 10) affects the oxygen ion activity in the opposite direction and leads to the occurrence of a maximum.

Our cells are not amenable to exact thermodynamic treatment since they have liquid junctions and the junction potentials are not known. On the other hand, it has been found that the junction potentials in cells involving molten salts are usually very small and can be neglected for an approximate quantitative treatment.[13] In our case it may be reasoned that the junction potentials are in all probability not larger than the reproducibility of the measurements (5 mv.).

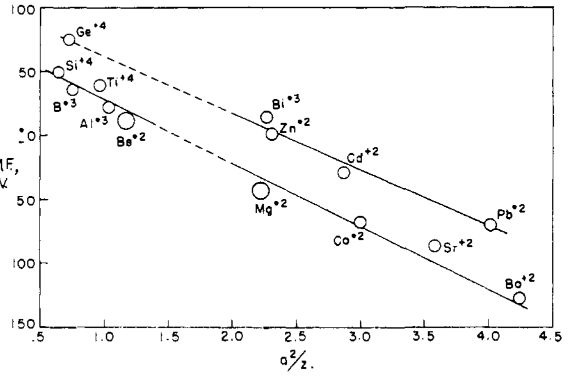

Fig. 5.—Potentials *vs.* a^2/z values.

If we neglect the junction potentials and consider the oxygen ion activity of the standard glass as our "standard state," we can calculate the oxygen ion activity for every solution from the Nernst equation

$$\text{e.m.f.} = -\frac{RT}{nF} \ln O^{-2}_{\text{sol.}}$$

For the glasses whose potentials fall on the main hyperbolic curve, a more general treatment can be attempted. If we plot these potentials against the inverse z/a^2 values we obtain the straight line of Fig. 5, which is expressed by the empirical equation

$$\text{e.m.f.} = 0.050a^2/z + 0.079$$

Combining this with the first equation and calculating the constants, we have

$$\ln O^{-2}_{\text{sol.}} = 0.429\, a^2/z - 0.678$$

Of course, this equation is true only for our particular solvent at 900°. It is interesting to find the Nernst equation applicable here, but in order to obtain any deeper insight into the nature of the constants evaluated above it would be necessary to conduct similar investigations in a series of lead silicates of different PbO : SiO_2 ratios and to measure the potentials as a function of temperature.

Acknowledgment.—The authors deeply appreciate the assistance of the Mallinckrodt Fund at Harvard University in obtaining reagents and materials.

[13] L. Holub, F. Neubert and F. Sauerwald, *Z. physik. Chem.*, **A174**, 161 (1935).

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Solubilities of Sulfur Hexafluoride in Water and of the Rare Gases, Sulfur Hexafluoride and Osmium Tetroxide in Nitromethane[1]

BY HAROLD L. FRIEDMAN

RECEIVED FEBRUARY 20, 1954

The following gas solubilities (Ostwald coefficients) have been determined at 25° with an accuracy of about 3%: in water, SF_6 = 0.0055; in nitromethane, He = 0.0175, Ne = 0.0245, A = 0.145, Kr = 0.380, Xe = 1.14, SF_6 = 0.377, OsO_4 = 1100. The OsO_4 value was obtained indirectly by studying the partition of OsO_4 in nitromethane–water mixtures. The solubilities of SF_6 also have been measured at lower temperatures. Sulfur hexafluoride exhibits the lowest solubility in water at 25° of any gas known, owing to an abnormally large entropy decrease upon forming the solution. Rough agreement with the regular solution theory is exhibited by these substances in nitromethane. It is found that the 25° solubilities of the rare gases in a variety of solvents, including water, may be correlated by the equation $\log x = a + bg$ where x is the solubility and a and b depend only upon the solvent and g depends only upon the gas. This correlation is accurate to ±5% in the solubility.

In connection with a study of the free energy of transfer of electrolytes from water to nitromethane[2] it seemed of interest to obtain for comparison the free energies of transfer of neutral molecules similar in size and structure to the ions of the electrolytes. Some solubilities which were obtained for this purpose are reported here (Table I).

The solubilities of helium and argon in water were obtained to check the method used here.

Aqueous Solutions of Sulfur Hexafluoride.—It is noteworthy that at 25° SF_6 has the lowest solubility in water reported for any gas. Thus the Ostwald coefficients for some other solutes in water at 25° are: N_2 = 0.016,[3] CH_4 = 0.033,[3] C_2H_6 = 0.045,[3]

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[1] This work was supported by the Atomic Energy Commission.

[2] H. L. Friedman and G. L. Haugen, THIS JOURNAL, **76**, 2060 (1954).

[3] J. H. Hildebrand and R. L. Scott, "The Solubility of Non-Electrolytes," Reinhold Publ. Corp., New York, N. Y., 1950, Chapt. XV.

TABLE I

OSTWALD SOLUBILITY COEFFICIENTS

Solvent	Gas	Temp., °C.	$l_{\text{expt.}}$		$l_{\text{calcd.}}$ or ($l_{\text{lit.}}$)
				Avg.	
H_2O	He	24.85	0.0091, 0.0093, 0.0096	0.0093	(0.0095)[a]
H_2O	A	24.85	.0342, 0.0338	.0340	(.0343)[a]
H_2O	A	14.8	.0404, 0.0403, 0.0407	.0405	(.0391)[a]
H_2O	SF_6	24.85	.0054, 0.0053, 0.0055, 0.0058	.0055	
H_2O	SF_6	14.9	.0076, 0.0076	.0076	
H_2O	SF_6	0.1	.0147, 0.0147	.0147	
H_2O satd. with $MeNO_2$	He	24.85	.0089, 0.0084, 0.0092	.0088	
H_2O satd. with $MeNO_2$	A	24.85	.0317, 0.0317	.0317	
H_2O satd. with $MeNO_2$	SF_6	24.85	.0058, 0.0053	.0055	
$MeNO_2$ satd. with H_2O	He	24.85	.0170, 0.0163	.0167	
$MeNO_2$ satd. with H_2O	A	24.85	.139, 0.141	.140	
$MeNO_2$	He	24.85	.0169, 0.0176, 0.0177	.0175	
$MeNO_2$	Ne	24.85	.0241, 0.0249	.0245	.093
$MeNO_2$	A	24.85	.138, 0.146, 0.146	.145	.21
$MeNO_2$	Kr	24.85	.381, 0.378	.380	.49
$MeNO_2$	Xe	24.85	1.15, 1.11, 1.15	1.14	1.6
$MeNO_2$	N_2	24.85	0.091	0.091	0.057
$MeNO_2$	SF_6	24.85	.374, 0.380	.377	.50
$MeNO_2$	SF_6	19.35	.354, 0.364, 0.369	.363	
$MeNO_2$	SF_6	0.1	.374, 0.369	.372	
$MeNO_2$	OsO_4	24.85	Indirect	1100	39000

[a] A. Lannung, THIS JOURNAL, **52**, 68 (1934).

Xe = 0.118,[4] Hg = 1,[5] C_6H_6 = 4.5,[6] $C_{10}H_8$ = 46[6] and OsO_4 = 78.[7] The solubility of SF_6 in water is too low to allow a careful investigation of its temperature coefficient with the apparatus used here, but the data obtained lead to an estimate of $\Delta H = -7$ kcal./mole and $\Delta S = -50$ e.u. for the transfer of SF_6 from the gas phase at 1 atm. to hypothetical unit mole fraction solution in water. Comparison with a Barclay–Butler plot for aqueous solution[6,8] shows that this ΔS is about 10 e.u. more negative than normal for this ΔH. Powell and Latimer[9] proposed an empirical relation between the partial molal entropies of non-electrolytes in aqueous solution and the molal volume of the pure liquid solute. For the standard states employed here this requires that $\Delta S = -24 - 0.22V_m = -41$ e.u., for SF_6 in water, again indicating that the entropy of solution of this gas is too negative by about 10 units. On the other hand the enthalpy of solution in water is more negative than the enthalpy of condensation (about -4 kcal.[10]) or the enthalpy of solution in nitromethane (0 ± 1 kcal.), suggesting that a specific interaction with the water, perhaps through hydrogen bonding, may be responsible for the abnormal entropy change. It would be of interest to obtain more accurate solubility data over a temperature range to see whether the partial molal heat capacities give evidence of "iceberg" formation.[6,8]

Nitromethane–Water Mixtures.—The data show that the effects upon solubility of saturating water with nitromethane (4 mole per cent. CH_3NO_2)[11] and nitromethane with water (12 mole per cent. H_2O)[11] are small compared with the effect of substituting one solvent for the other. Assuming that this holds also for OsO_4 as a solute, the results of the measurements of the partition of OsO_4 in nitromethane–water mixtures (Fig. 1) may be used to estimate its solubility in nitromethane, since its solubility in water and volatility are known.[7]

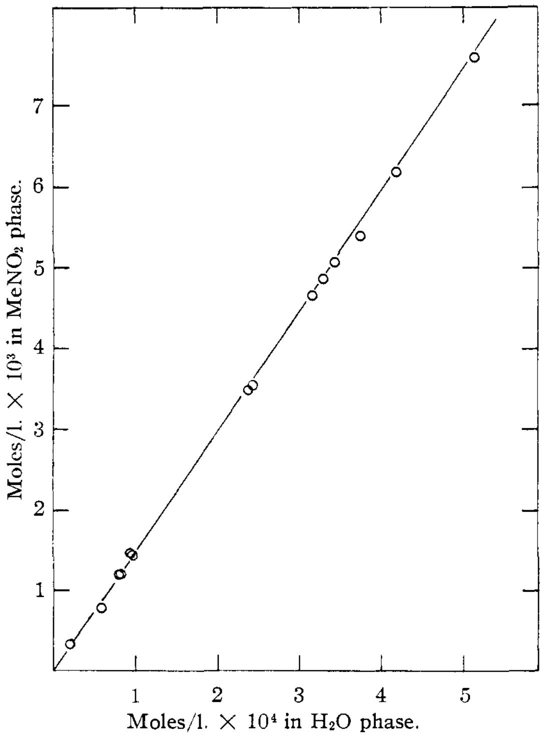

Fig. 1.—The partition of OsO_4 in water–nitromethane mixtures at 25°.

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(4) S. Valentiner, *Z. Physik*, **42**, 253 (1927).

(5) A. Stock, *Z. anorg. allgem. Chem.*, **217**, 241 (1934).

(6) E. F. G. Herington, THIS JOURNAL, **73**, 5883 (1951).

(7) L. H. Anderson and D. M. Yost, *ibid.*, **60**, 1822 (1938).

(8) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

(9) R. E. Powell and W. M. Latimer, *ibid.*, **19**, 1139 (1951), eq. 10.

(10) H. C. Miller, L. S. Verdelli and J. F. Gall, *Ind. Eng. Chem.*, **43**, 1126 (1951).

(11) R. M. Corelli, *C. A.*, **46**, 3370e (1952).

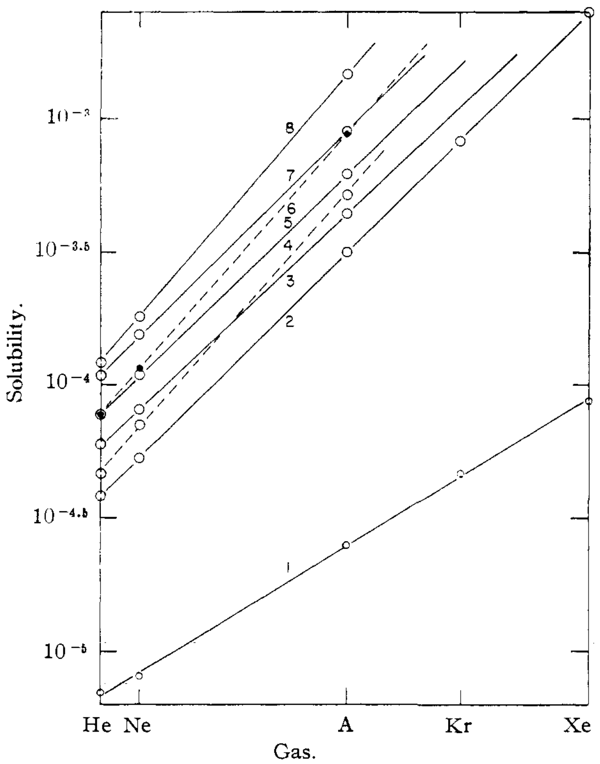

Fig. 2.—Solubilities of the rare gases in various solvents. Solubilities are in mole fraction units at 25° and 1 atm. partial pressure of gas. The scale of abscissa is chosen to make the nitromethane curve linear. The radii of the larger circles correspond to a 5% change in solubility. Solvents: 1, H_2O; 2, CH_3NO_2; 3, CH_3OH; 4, cyclo-C_6H_{11}-OH; 5, C_2H_5OH; 6, C_6H_6; 7, $(CH_3)_2CO$; 8, cyclo-C_6H_{12}. Data not from this paper are from ref. *a*, Table I, or from ref. 4.

Nitromethane Solutions.—The Trouton's constant for nitromethane is 24. Both this and the application of the Hildebrand rule indicate that this liquid is intermediate between the most associated liquids, the alcohols and water, and the "normal liquids." It is of interest to see how far the regular solution theory, as modified by Gjaldbaek and Hildebrand[12] to allow for non-ideal entropy of mixing arising from differences in molar volume, will lead to solubilities in agreement with the measured ones. The entries in the last column of Table I have been calculated in this way, using the solubility parameters and partial molal volumes proposed by Hildebrand and Scott.[13,14]

The calculated solubilities are for the most part 30 to 50% larger than the experimental values, which must be considered excellent agreement in view of the fact that none of the parameters required in the calculation has been evaluated from solubility measurements. However, a calculation of the solubility of N_2 in nitromethane, using parameters which Gjaldbaek and Hildebrand obtained from solubility measurements,[12] leads to an Ostwald coefficient of only 0.006. The measurement of the solubility of N_2 reported in Table I was made to confirm that this was unreasonable.

A correlation of the solubilities of the rare gases in various solvents is provided by Fig. 2. Evidently the solubility (mole fraction at 1 atm. partial pressure) of a rare gas is given by the equation

$$\log x = a + bg \qquad (1)$$

where *a* and *b* depend only upon the solvent and *g* depends only upon the gas. The regular solution theory predicts a somewhat different dependence

$$\log x = -\log p^0 - v_2(\delta_1 - \delta_2)^2/4.57T \qquad (2)$$

This is inconsistent with eq. 1 unless v_2 is strongly dependent upon δ_1. The data available indicate that this is not the case for other gases.[3] It is most surprising that the applicability of eq. 1 extends to the hydroxylic solvents in which it is believed that structure plays an important role in determining solubility. This suggests that there is no sudden change in structural effects in water on passing from one rare gas to the next in order of size.

Hildebrand and Scott[3] cite the relative ease of transfer of helium from organic solvent to water, as compared with other gases, and offer this as evidence that He atoms fit into holes in the water structure. However it is apparent from Fig. 2 that this arises because water has a smaller *b* parameter than the organic solvents (*i.e.*, the slope of the curve is smaller), and while this difference in *b* may have a structural cause, it cannot be something peculiar to the interaction of He and water.

It appears that the empirical correlation of Fig. 2 will be valuable for the calculation of the solubilities of the remaining rare gases in a solvent after the solubilities of two of them have been determined experimentally or, in favorable cases, by the application of the regular solution theory. Equation 1 is also consistent with the solubilities of Rn in H_2O, C_6H_6 and $(CH_3)_2CO$ although these have not been shown in the figure. The data on the solubilities of N_2 and CH_4 also have been tested in this way and found to fit within 12% except for solubilities in water.

Experimental

Materials.—Conductivity water and redistilled nitromethane were employed as solvents. Where necessary, the nitromethane was dried by filtering at −20°. He, Ne, Kr and Xe were reagent grade products of the Air Reduction Co., at least 99.8% pure according to mass spectrometer analyses by the manufacturer. Argon was Linde Air Products Spectro grade. N_2 was purified by passing over CaH_2 and CoO. SF_6 (Mathieson) was freed from a more volatile impurity by fractional condensation at −190° to give a product having a vapor pressure at −78° of 275–276 mm. in good agreement with the literature value of 275.5 mm.[15] The product was tensiometrically homogeneous. A standard solution of OsO_4 was prepared by dissolving a weighed portion of the commercial C.P. product in 0.004 *M* Cl_2 solution to give a solution 0.02 *M* in OsO_4.

Gas Solubility Measurements.—The method was essentially that employed by Eucken and Herzberg.[16] Instead of shaking the saturation vessel to reach equilibrium, a magnetically stirred, jacketed vessel[17] was used. This was connected by a short capillary tube to the buret. Instead of balancing the gas pressure against the atmosphere

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[12] J. Chr. Gjaldbaek and J. H. Hildebrand, THIS JOURNAL, **71**, 3147 (1949), eq. 2.

[13] Ref. 3, Appendix 1.

[14] The molal volumes listed by H. and S. were taken as the partial molal volumes in solution. The ideal solubilities of the rare gases were calculated by extrapolating the vapor pressures to 298°K.

[15] W. C. Schumb, *Ind. Eng. Chem.*, **39**, 421 (1947).

[16] A. Eucken and G. Herzberg, *Z. physik. Chem.*, **195**, 1 (1950).

[17] W. K. Wilmarth and C. F. Baes, *J. Chem. Phys.*, **20**, 116 (1952).

in the usual way, it was balanced against a column of mercury in a barometer with electrical contacts to indicate, by a neon light, the attainment of the preset pressure, about 70 cm. A change of 0.01 ml. in the position of the mercury meniscus in the 25-ml. buret was easily detected with this arrangement. The apparatus would be more satisfactory, however, if the entire gas volume were thermostated.

The solvent was degassed by alternately opening to the vacuum pump for 5–15 sec. and then stirring very rapidly to produce cavitation. This was repeated 5 to 10 times. In the solubility measurement itself, gas which had been previously saturated with solvent vapor, was admitted to the saturation vessel, holding about 80 ml. of soln., and with 5 to 10 ml. remaining space, and volume–time measurements were taken and extrapolated back to the time the gas was admitted. Then the stirrer was turned on and driven very fast, producing a slightly (*ca.* 1%) supersaturated solution. The approach to equilibrium was then followed from each direction while stirring as rapidly as possible without producing cavitation and bubbles. The Ostwald solubility coefficient was calculated from the eq. $l = V_g T_s / V_s T_g$ where V_g and V_s are volumes of gas absorbed (the volume change in the buret) and volume of solution, respectively, and T_s and T_g are the absolute temperatures of the solution and of the gas in the buret.

The degree of internal consistency of the results and of agreement with the work of Lannung indicates that the measured Ostwald coefficients are accurate within 3%.

The Partition of OsO_4.—Nitromethane which had been washed with acid and Cl_2 water was equilibrated at 25° with aqueous solutions of OsO_4 containing added acid and Cl_2. The acid and Cl_2 were found to prevent the reduction of OsO_4 by trace impurities in the system. Variation of the amounts of added acid and Cl_2 up to the concentrations employed (0.05 and 0.005 *M*, respectively) had no effect upon the partition ratio within the accuracy of these measurements. In some cases equilibrium was approached from the opposite direction with consistent results.

Aliquots of the equilibrated phases were added to 3.0 ml. of a mixture of 50 ml. of saturated thiourea solution and 200 ml. of 6 *M* HCl and made up to 5.00 ml. with water. Five to ten minutes after mixing the two solutions from a single partition expt. were examined with a Beckman spectrophotometer (DU) at the absorption maximum of the pink complex[18] formed by the action of the thiourea on the OsO_4. The molar decadic extinction coefficients at the maxima were: at 481 $m\mu$, ϵ 3850, and at 535 $m\mu$, ϵ 2890. These were somewhat variable with the age of the reagent solution and the time of standing after the color developed, but aliquots were taken in such a way that nearly the same intensity of color developed in the analysis of each phase and, incidentally, the nitromethane concentrations were roughly the same in the resulting solutions. In this way the analytical errors partly cancel out in calculating the partition coefficients. The 481 $m\mu$ results are presented in Fig. 1. The measured partition ratio is 14.9 = molarity of $MeNO_2$ layer/molarity of H_2O layer. The measurements at the longer wave length gave the same result.

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[18] F. J. Welcher, "Organic Analytical Reagents," IV, D. Van Nostrand Co., Inc., New York, N. Y., 1948, p. 183.

LOS ANGELES, CALIFORNIA

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

Reactions of Some Metal Salts with Alkali Superoxides in Liquid Ammonia

BY DALE L. SCHECHTER AND JACOB KLEINBERG

RECEIVED FEBRUARY 8, 1954

The reactions of a variety of anhydrous metal salts with potassium and sodium superoxides in liquid ammonia medium have been studied. Where the reactants are brought together in stoichiometric proportions required for metathesis and reaction occurs, the superoxide ion is unstable and solid superoxides cannot be isolated. Lithium, magnesium, calcium, cadmium and zinc nitrates are converted to solid products containing large proportions of the corresponding peroxides. Except for lithium and calcium peroxides, which have been previously prepared in small yield by direct oxidation of liquid ammonia solutions of the metals, this is the first time that these peroxides have been prepared in the anhydrous state. Decomposition of peroxide, followed by ammonolysis of the "normal" oxide, and oxidation of amide to nitrite and hydroxide, also occur. Aluminum chloride tetraammoniate reacts with sodium superoxide in a 1:6 mole ratio to yield a product containing sodium, aluminum and "non-reducible anion base" in the same ratio as that found in Na_3AlO_3. Copper(II) nitrate tetraammoniate reacts with either sodium or potassium superoxide to form products consisting largely of monoxide, hydroxide and copper(II) amide.

Attempts in this Laboratory to prepare barium and strontium superoxides in liquid ammonia by metathetic reactions involving alkali metal superoxides, although unsuccessful, have led to the isolation of a mixed superoxide–peroxide of the composition ($2K^+$, Ba^{++}, $2O_2^-$, $O_2^=$), and also to the formation of anhydrous barium and strontium peroxides of relatively high purity.[1] The present communication describes the results of reactions in liquid ammonia between a variety of anhydrous salts [$LiNO_3$, $Ca(NO_3)_2$, $Mg(NO_3)_2 \cdot 6NH_3$, $Zn(NO_3)_2 \cdot 4NH_3$, $Cd(NO_3)_2 \cdot 6NH_3$, $AlCl_3 \cdot 4NH_3$ and $Cu(NO_3)_2 \cdot 4NH_3$] and sodium and potassium superoxides. In every case where the reactants are mixed in the stoichiometric proportions necessary for metathesis and reaction occurs, the superoxide ion is unstable and decomposes with the liberation of oxygen. Although no new superoxides or mixed superoxides–peroxides have been obtained, solid products containing large proportions of the anhydrous peroxides of lithium, magnesium, calcium, cadmium and zinc have been isolated.

Experimental

Materials.—"Refrigeration grade" Spencer ammonia was dried before use by condensation into a stainless steel tank containing metallic sodium. The head of this tank, which had an ordinary needle valve as outlet, was removable, permitting the addition of the drying agent. The potassium and sodium superoxides employed (98 and 94% purity, respectively) were supplied by the Callery Chemical Co., Callery, Pa. Baker Analyzed grade anhydrous lithium nitrate was used without further purification. Anhydrous calcium nitrate was obtained by dehydration of the tetrahydrate at 130–140° for 4 hr., followed by heating in a vacuum oven at 70° and 0.3 mm. pressure for 19 hr. Aluminum chloride tetraammoniate was prepared by passage of a slow stream of mixture of gaseous ammonia and dry nitrogen (roughly one volume to five) through an erlenmeyer flask containing a few grams of Baker Analyzed anhydrous chloride. The flask was immersed in a Dry Ice–cellosolve bath in order to dissipate the heat evolved in the ammoniation process and thereby inhibit the ammonolytic reaction.

The ammoniates of magnesium, zinc, cadmium and copper nitrates were all prepared from Baker Analyzed grade or the equivalent commercially available hydrated com-

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[1] E. Seyb, Jr., and J. Kleinberg, THIS JOURNAL, 73, 2308 (1951).