each case measurements at low humidities approached a constant value for high frequencies, and in the case of KCl the correct value for the dielectric constant is obtained under these conditions. Cooling the samples below 0° virtually eliminated all dielectric losses. Also the dielectric constant became frequency-independent and equal to the limiting high-frequency value. Attempts to measure the water uptake by the powders showed less than 0.1% by weight in $NaHCO_3$ for x_{H_2O} = 0.50 at 25°. It is concluded that the observed effects are due to the formation of electrically conducting films by the adsorption of water vapor. Further studies of the electrical properties of such films under more precisely defined experimental conditions should be of considerable interest in surface chemistry.

Acknowledgments.—I wish to acknowledge the stimulating discussions of my colleagues, particularly Professor W. M. Latimer, who pointed out the interest in this study, and the assistance of W. J. Potts, Fred Andrews, Floyd Momyer and David Schwartz in some of the preliminary studies.

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

A Study of the Hydrogen Chloride–Aluminum Chloride System

BY RYDEN L. RICHARDSON[1] AND SIDNEY W. BENSON

The hydrogen chloride–aluminum chloride system has been examined over a wide range of conditions by use of varied techniques. Pressure–composition isotherms at −78, 0 and 25° gave negative results as to formation of $HAlCl_4$. Weak physical adsorption and extremely low conductivity were noted. At 195° and ~1500 mm. deviations of all-vapor system from ideal behavior were so slight as to be questionable. Complete exchange of $^{36}_{17}Cl$ occurred at similarly elevated conditions but no exchange was detected at room temperature.

Introduction

Although the complex compound $HAlCl_4$ has been cited in proposed mechanisms for certain Friedel–Crafts reactions, the existence of this complex has never been experimentally verified. Several investigators[2,3,4] have found that aluminum chloride and hydrogen chloride decidedly resist combination. Fairly recent studies[5,6] have cast doubt upon a kinetic investigation[7] which appeared to substantiate existence of the bromine analog, $HAlBr_4$.

The present paper describes several experiments designed to detect either complex formation or intermolecular attraction within the hydrogen chloride–aluminum chloride system. Accordingly, measurements have been devoted to phase equilibria, solubility, conductivity, P–V–T behavior and isotope exchange. The data collectively apply to a temperature range of −80 to 220° and a pressure range of 0 to 1200 mm.

Experimental

Materials.—Reagent-grade anhydrous aluminum chloride was further purified by fractionation in an all-Pyrex system pressured to 1.2 atm. with dry nitrogen. Three samplings of product, sealed in evacuated capillary tubes, had an average m.p. of 193.7 ± 0.1° within 0.8° range (reported,[8] 192.6°).

Hydrogen chloride from a commercial cylinder was purified by repeated batch-wise fractionation in a U-tube train. Purity of four samples was checked by vapor pressure measurements in −110 to 86° range; these measurements had a mean deviation of < 2% from data cited in Landolt–Börnstein.[9]

Radioactive hydrogen chloride was generated by a mixture of C.P. concentrated sulfuric acid and radio-potassium chloride ($^{36}_{17}Cl$, Oak Ridge Laboratories). Purification of the evolved gas was carried out in essentially the same manner and degree as described for unactive species.

Phase Equilibrium.—Data for pressure *vs.* composition isotherms at −78, 0 and 25° were obtained by contacting 0.4–0.6 g. of anhydrous aluminum chloride with hydrogen chloride in a conventional adsorption apparatus.[10] Temperature measurements with a toluene thermometer were occasionally checked by ammonia or carbon dioxide vapor pressure thermometers; mixtures of Dry Ice–acetone or water–ice served as cooling baths. Pressure equilibrium was instantaneously attained and no hysteresis was observed. The amount of aluminum chloride was volumetrically determined at the end of each run series by use of silver nitrate and dichlorofluorescein.

Solubility.—During phase equilibrium measurements at −78°, hydrogen chloride was condensed to give 2–4 ml. of liquid in contact with excess of solid aluminum chloride. Six observations on two different samples indicated a lowering of vapor pressure. Temperatures were checked with ammonia and carbon dioxide vapor pressure thermometers. A third sample, also used for conductivity measurements, was equilibrated for 24 hours at −81° with occasional agitation; vapor pressure lowering of the same magnitude was observed. Flaming and sustained evacuation prior to introduction of materials precluded water as the cause of such an effect.

Conductivity.—With exception of platinum electrodes and tungsten leads, the conductivity cell was of all-Pyrex construction. Cell contents were magnetically stirred and occasionally lead shields from the cell were flamed to prevent moisture condensation. A Jones bridge[11] measured the resistance at 1000 cycles/sec. No frequency effects (400 cycles/sec.) were noted.

Oven Bulb Apparatus.—This apparatus included an air-bath, oven-bulb (600 ml.), null-detector,[12] mercury manometer, three copper–constantan thermocouples and a L. & N. potentiometer (Model #8662). Materials sealed in the oven-bulb system contacted Pyrex surfaces only. Upon

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[1] Filtrol Corporation, Vernon. California.

[2] R. Schwartz and G. Meyer. *Z. anorg. allgem. Chem.*, **166**, 190 (1927).

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[6] C. M. Fontana and R. J. Herold, *ibid.*, **70**, 2881 (1948).

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[8] A. Smits, J. L. Meyering and M. A. Kamerans. *Proc. Acad. Sci. Amsterdam*, **34**, 1327 (1931).

[9] Landolt–Börnstein, "Phys. Tabellen." Auflage V. Vol. II. 1923. p. 1343.

[10] R. N. Pease, THIS JOURNAL, **45**, 1197 (1923).

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slow heating or cooling of the fan-circulated air-bath within electrically heated oven, thermocouples (5 cm. closest approach) at three points contiguous with oven-bulb indicated temperature differences of 0.3° or less. Calibrations (ice, steam and tin) revealed thermocouples accurate to ±0.1°. Vapor hold-up of lead line and null-detector sections maintained 150° > oven temperature, represented about 1% of oven-bulb volume.

After evacuating the oven-bulb system and charging lines for >3 hours at ~ 250°, purified aluminum chloride was sublimed into the oven-bulb and therein sealed off after exhaustive pumping at room temperature. Data from ensuing 45-hour calibration run were consistent with precision of temperature measurements. (This fact was also confirmed by later calibration with resublimed iodine.)

Having calibrated apparatus with aluminum chloride, the charging line again was connected by torch to seal-extension of oven bulb. After flaming and pumping, hydrogen chloride was introduced by customary use of the magnetic hammer and break-off tip. The oven bulb system with contents frozen by liquid nitrogen was pumped and sealed off, preparatory to *P–V–T* run.

Exchange Measurements.—Specific activities of radioactive hydrogen chloride were measured before and after contact with unexchanged aluminum chloride in the oven bulb apparatus. Gas was sampled at room temperature, always filling the jacket of counter tube with fixed molar quantity of gas. A 20–80 mole % mixture of ethanol and argon, respectively, filled the ionization chamber of the counter tube (the counter tube was a special model manufactured by Eck and Krebs Company). The counter tube circuit included a Berkeley Decimal Geiger-Müller Scaler (Model 1000-B) and a control timer of $^1/_{100}$ minute accuracy (Standard Electric Time Co., Springfield, Mass.). An applied voltage of 1.05 kv., selected from plateau of counting rate *vs.* applied voltage, was used exclusively for all counting work. When filled with standard sample of exchanged gas (100 mm. at 17.8°), the light-shielded tube indicated uncorrected activity of 580 ± 12 counts/min. No other corrections than background count were applied.

Results and Discussion

Phase Equilibrium.—The pressure *vs.* composition isotherms in Fig. 1 are unquestionably void of pressure plateaus corresponding to solid addition compounds formed by gaseous hydrogen chloride and solid aluminum chloride. If addition compounds exist at 0 and 25°, their dissociation pressures must exceed 1185 and 1290 mm., respectively. In particular, the stability of solid $HAlCl_4$ at 25° in terms of the equilibrium

$$2HAlCl_4(s) = 2HCl(g) + Al_2Cl_6(s)$$

must comply with values for K_p and $\Delta F°_{298}$ which exceed 2.89 atm.[2] and −628 cal., respectively. (These limiting values involve assumption that fugacity of hydrogen chloride is equal to its pressure.)

Other features to be noted: (1) Restricted values ($\leqslant 0.02$) of abscissas in Fig. 1 point to feeble adsorption. (2) At 0° and 963 mm. the adsorption of hydrogen chloride by powdered anhydrous aluminum chloride was <2 cc. S.T.P./g. Al_2Cl_6. (3) Essentially the same extent of adsorption was observed with an empty Pyrex sample tube.

Solubility.—Observation of vapor pressure lowering of ~30 mm. over interval of −77 to −81° indicated the observed water-clear liquid phase to be a solution of aluminum chloride in hydrogen chloride. Using Raoult's law, the solubility at −78° was estimated as 3.8 ± 0.9 mole per cent. (Use of Raoult's law should not be objectionable on basis of ionization because extremely low conductivities were displayed by the system.)

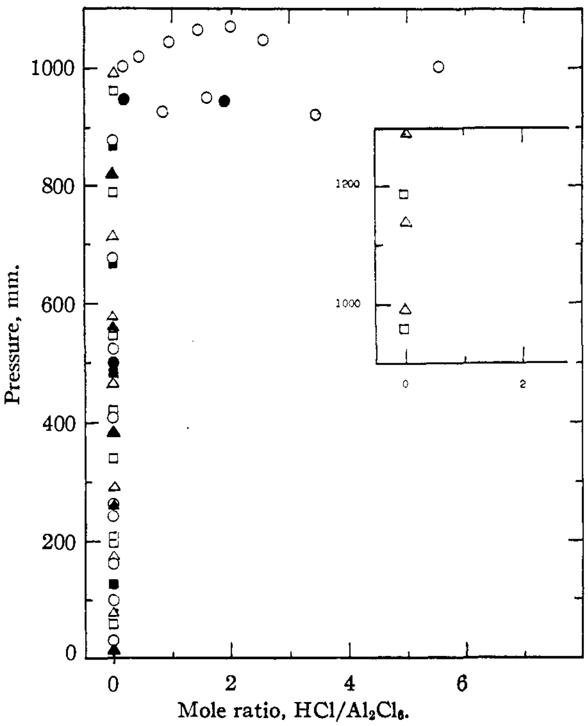

Fig. 1.—Pressure *vs.* composition isotherms: (○, ●), adsorption, desorption at −78°; (□, ■), adsorption, desorption at 0°; (△, ▲), adsorption, desorption at 25°.

One should note that: (1) Application of data to the solubility equation[13] leads to 9 ± 3 kcal. for ΔH_f, the molar heat of fusion; (2) this value of ΔH_f is in approximate thermodynamic agreement with 17.0 kcal. reported at 193° by Fischer and Rahlfs[14]; (3) taking 17.0 kcal. as ΔH_f at 193°, assuming existence of dimeric species only, and referring to the heat capacity equation of Kelley,[15] application of the Kirchhoff relation predicts that ΔH_f near −78° should be ~12 kcal.

Conductivity.—Conductivity measurements on saturated solution of aluminum chloride in hydrogen chloride embraced nine observations and equilibration periods of 0.3 to 21.5 hours. A small increase in conductivity developed upon standing (4.4×10^{-7} to 6.0×10^{-7} mho/cm.). This effect has been noted[16] with hydrogen chloride at −85°; in 24 hours conductivity increased from 0.7×10^{-8} to 5.4×10^{-8} mho/cm. The proximity of the latter value to (5.5 ± 0.5) (10^{-7}) mho/cm. selected for the aluminum chloride–hydrogen chloride system at −77° immediately suggests inappreciable ionization.[17] If $HAlCl_4$ does exist appreciably in this system, it does not appear to have an acid strength sufficient to force a proton onto hydrogen chloride.

P–V–T Behavior.—In principle, the experimental method involved pressure and temperature measurements on fixed amounts of the components before and after mixing in an all-Pyrex oven bulb apparatus of constant volume. A calibra-

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[13] $\log\left(\frac{x_1}{x_2}\right) = \frac{\Delta H_f}{2.30R}\left(\frac{T_1 - T_2}{T_1T_2}\right)$

[14] W. Fischer and O. Rahlfs, *Z. anorg. allgem. Chem.*, **205**, 37 (1932).

[15] K. K. Kelley, *Bur. Mines Bull.*, **371**, 9 (1934).

[16] G. Glockler and R. Peck, *J. Chem. Phys.*, **4**, 658 (1936).

[17] Conservative approximations through use of Walden's rule indicate that degree of ionization probably does not exceed 10^{-1}%.

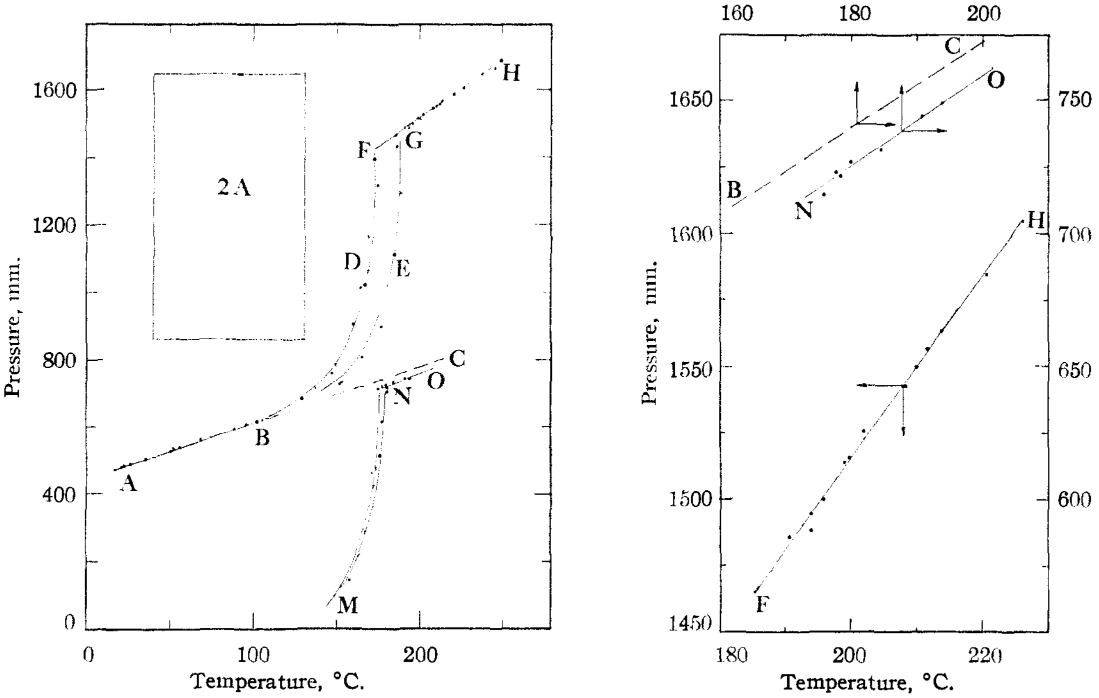

Fig. 2 and 2A insert.—Pressure *vs.* temperature curve from P- V-T run of 19-hr. duration. (Run 1): AB, heating or cooling $HCl(g) + Al_2Cl_6(s)$; BC, extrapolation for HCl(g); BEG, heating $HCl(g) + Al_2Cl_6(g) + Al_2Cl_6(s)$; FGH, heating or cooling $HCl(g) + Al_2Cl_6(g)$; FDB, cooling $HCl(g) + Al_2Cl_6(g) + Al_2Cl_6(s)$; MN, heating or cooling $Al_2Cl_6(g) + Al_2Cl_6(s)$; NO, heating or cooling $Al_2Cl_6(g)$.

tion run was made with purified aluminum chloride in order to check accuracy of pressure and temperature measurements obtained with this apparatus; vapor pressure data had a root mean square deviation of 3.1% about

$$\log P_{\text{mm.}} = -(5.890)(10^3)/T + 15.857$$

for range of 20–1200 mm. These results agree with recent investigations[18,19] but grossly disagree with Maier's earlier reported data.[20] (Maier's data, believed to be in error due to a diffusion effect noted in this study, are cited in both "International Critical Tables" and Landolt–Börnstein "Tabellen.")

Subsequent introduction of hydrogen chloride marked the beginning of P–V–T runs having varied duration (19, 68 and 530 hours). Figure 2 pertains to Run 1, which was of 19 hours duration. Data from this run and others not reported reveal that a hysteresis loop (BDFGEB) coexisted with the heterogeneous system only and enclosed an area which became vanishingly small as the run duration increased. Such an effect is attributed to diffusion rather than heat transfer because comparable behavior was not displayed by the aluminum chloride alone.

Measurements on the all-vapor system, embracing data of segments GH, BC and NO in Fig. 2, point to a deviation from ideal behavior by an amount almost twice the maximum experimental error. Insert of Fig. 2 reveals that at 190° the sum of separately measured components was 1498 ± 3 mm. but the total pressure of the mixture was only 1481 ± 2 mm. These data were corrected for effect of (1) expansion of oven bulb, (2) change in oven bulb volume after seal-off operation, and (3) increase in volume of vapor phase attending sublimation of aluminum chloride. Nevertheless, the modified data[21] indicated the pressure of the real mixture was 12 ± 7 mm. or 0.8 ± 0.5% less than the ideal mixture. If one assumes this decrease to be caused by the interaction

$$2HCl(g) + Al_2Cl_6(g) = 2HAlCl_4(g)$$

and the fugacity of each species equal to its partial pressure, then the 12 ± 7 mm. deviation limits K_p to some value between 2×10^{-4} and 3×10^{-3} atm.$^{-1}$. Alternatively, $\Delta F°_{463} = 6.5 \pm 1.3$ kcal.

Isotope Exchange.—As can be seen from the data in Table I, contrasting results were obtained by exchange runs made at elevated and room temperatures. The run at elevated temperature, having a duration of 76 hours and reaching a maximum temperature of 213°, produced a 84 ± 4% decrease in specific activity of the radioactive hydrogen chloride gas. On the other hand, two runs made at room temperature produced no detectable decrease in specific activity of the gas. A calculation has been made with the assumption that the next exchange is

$$HCl^*(g) + Al_2Cl_6(g) = Al_2Cl_5Cl^* + HCl(g)$$

wherein Cl* is identical with ${}^{36}_{17}Cl$. Applying data of Run C, it has been found that the 84 ± 4% decrease in specific activity corresponds to com-

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[18] A. Smits, J. L. Meyering and M. A. Kamerans, *Proc. Acad. Sci. Amsterdam*, **35**, 193 (1932).

[19] W. Fischer and O. Rahlfs, *Z. anorg. allgem. Chem.*, **205**, 24 (1932).

[20] C. G. Maier, *Bur. of Mines Tech. Paper*, **360**, 1 (1925).

[21] Pressure of hydrogen chloride, 755 ± 3 mm.; pressure of aluminum chloride, 742 ± 1 mm.; pressure of real mixture, 1485 ± 3 mm.

TABLE I

Run	A	B	C
Duration, hr.	1.0 ± 0.2	12.0 ± 0.2	76.0 ± 0.5
Temp. range, °C.	25 ± 2	21 ± 2	20–215
Hydrogen chloride partial pressure, mm.	87 ± 1	198 ± 2	123–213
Aluminum chloride partial pressure, mm.	0	0	0–162
Initial specific activ. of HCl gas $\frac{\text{counts}}{\text{min. mole}}$	508 ± 15	508 ± 15	521 ± 8
Final specific activ. of HCl gas $\frac{\text{counts}}{\text{min. mole}}$	500 ± 15	505 ± 7	86 ± 4
Decrease in sp. activ. of HCl gas, %	<exptl. error	<exptl. error	84 ± 4

plete exchange. This fact points to the possible existence of $HAlCl_4$ but it does not prove its existence, since there are other conceivable paths for exchange.

Taken as a whole, the findings of this research present the following picture in regard to compound-formation in the system studied. At lower temperatures there is absolutely no evidence of chemical reaction. This follows from the absence of pressure plateaus concerning phase equilibria measurements and no decrease in specific activity of the gas during exchange runs at room temperature. But at higher temperatures, creating the all-vapor system and allowing for a slight dissociation of the gaseous aluminum chloride dimer, the extent of interaction is so small that it is questionable. This follows from the small departure from ideality observed during *P–V–T* investigation and the complete exchange observed for the only exchange run involving elevated temperatures.

Acknowledgments.—Courtesies have been extended by Dr. A. B. Burg, Dr. K. J. Mysels, Dr. A. W. Adamson and especially the Filtrol Corporation. Valuable contribution has been made by the late Kenneth P. Warren, who constructed the high temperature oven, and Mr. J. K. Fogo.

VERNON, CALIF. RECEIVED AUGUST 24, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMICAL ENGINEERING, GEORGIA INSTITUTE OF TECHNOLOGY]

The Heat Content, Specific Heat and Entropy of La_2O_3, Pr_6O_{11} and Nd_2O_3 Between 30 and 900°[1,2]

BY J. O. BLOMEKE[3] AND W. T. ZIEGLER

The heat contents of La_2O_3, Pr_6O_{11} and Nd_2O_3 have been measured from 30 to 900° using a copper aneroid calorimeter. Equations expressing the heat content, heat capacity and entropy of each of the rare earth oxides have been derived from the observed heat contents. As a means of testing the operational characteristics of the calorimeter, the heat content of a standard sample of α-Al_2O_3 was measured and found to compare favorably with values reported by other investigators.

Introduction

The rare earth elements and their compounds are a group of substances for which relatively few heat capacity data are available. This is due, in large measure, to the difficulty involved in separating them from one another in sufficiently pure form to warrant such measurements. Until recently, rare earth separations were most often carried out by the laborious process of fractional crystallization. The crystallization procedure has today been largely superseded by a more rapid, less arduous technique employing ion-exchange resins to effect these separations.[4]

This paper describes high-temperature heat content measurements made on samples of Pr_6O_{11} and Nd_2O_3 purified by means of the ion-exchange method and on a sample of La_2O_3 which was purchased commercially.

The calorimeter used for these measurements was calibrated electrically. Its operational characteristics were checked by measuring the heat content of α-Al_2O_3. The observed heat content for Al_2O_3 is compared with previous measurements from the literature.

Apparatus.—The calorimeter used for these measurements was patterned after one described by Southard.[5] This type of calorimeter consists of two main parts: a furnace in which the sample whose heat capacity is to be measured is brought to a constant temperature, and a calibrated copper block into which the sample is then dropped. From the temperature rise of the block and certain corrections characteristic of the particular arrangement used, the change in heat content of the substance can be obtained.

The winding of the present furnace was made of Nichrome V resistance wire. This winding limited the calorimeter to measurements below 1000°.

The capsule containing the sample was a 2.1 cm. × 2.1 cm. cylinder made of 0.2 mm. 90% platinum–10% rhodium alloy. The capsule had a tubular neck. Closure was made by sealing on a cap with fused gold.

The temperature of the capsule in the furnace was determined with a single-junction platinum, platinum–10% rhodium thermocouple, the junction of which was located just above but out of contact with the capsule. The thermocouple had recently been calibrated by the National Bureau of Standards. All e.m.f. measurements were made with a Leeds and Northrup Type K-2 potentiometer. Corrections to the observed e.m.f. readings of this thermocouple were applied on the basis of experiments carried out in which a second such thermocouple, placed inside an empty capsule suspended in the furnace, was compared with the measuring thermocouple at a number of furnace temperatures between

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[1] From a dissertation submitted by J. O. Blomeke to the Graduate Division of the Georgia Institute of Technology in partial fulfillment of the requirements for the Ph.D. degree (1950).

[2] Presented before the Physical and Inorganic Section of the Southwide Chemical Conference, Atlanta, Georgia, Oct. 16–18, 1950.

[3] Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[4] Symposium: "The Separation of Rare Earth, Fission Product and Other Metal Ions and Anions by Adsorption on Ion-Exchange Resins." THIS JOURNAL, **69**, 2769 (1947).

[5] J. C. Southard, THIS JOURNAL, **63**, 3142 (1941).