grams (about 50 c.c.) of ripe ovarian eggs of *Rana pipiens* were boiled in absolute alcohol and extracted with absolute ether and dried at 135°. They were then powdered and boiled in 200 c.c. distilled water slightly acidulated with acetic acid (free from salts) to coagulate the proteins, and filtered. The filtrate was evaporated down and both filtrate and precipitate charred and extracted and titrated for chlorides. The filtrate required 1.55 c.c. 1/10 normal $AgNO_3$, whereas the precipitate required but .2 c.c., which might be due to the small amount of filtrate held in the precipitate. It thus appears that very little if any salt was adsorbed. If all this chloride is NaCl it would make a .00756 molecular solution of the same volume as the egg. However, the osmotic pressure of the ovarian egg corresponds to that of a .166 normal NaCl solution. If this osmotic pressure is due chiefly to NaCl it must be confined to the watery phase which must equal .0455 or about 1/20 of the volume of the egg.

I found that frog's eggs lose NaCl continuously during their development in distilled water, hence they must be permeable to NaCl for some time after fertilization. This is in harmony with the fact that pure NaCl solutions are not so toxic to the frog's egg as to the eggs of many other animals. I found that those salt solutions which were toxic to fish eggs increased the permeability, but the fertilized frog's egg is already permeable.[10] Some of the older work on the effect of pure NaCl on the frog's egg might be objected to on the ground that the NaCl solution became contaminated by Ca contained in the egg jelly. Therefore I made a series of experiments in which small numbers of frog's eggs were washed for an hour in several liters of distilled water, and placed in several liters of pure $NaNO_3$ solution. Very dilute solutions were non-toxic. One tenth molecular solutions showed a toxic effect in 48 hours, but this may have been due to osmotic pressure, since the addition of 1.6 c.c. of a molecular $CaCl_2$ solution to the liter did not decrease the toxicity. The toxicity of all salts is not due entirely to osmotic pressure, since I found lithium salts to be slightly more toxic than sodium salts of same osmotic pressure.

All of the abnormalities in the lesser toxic salt solutions which I have observed or found in the literature, are characterized by a retardation or failure of the white pole to segment. This is also true of abnormalities produced by centrifugal force or other mechanical agents applied to the unsegmented egg. This unsegmented white pole prevents or retards the downgrowth of the black cell layer, and in extreme cases leads to the so-called "lithium larvæ." These embryos may regenerate and become normal tadpoles. The more toxic solutions prevent segmentation of the white pole and cause swelling of serous cavities (pericardium) and a separation or loosening up of the black cells, accompanied by death of some of these cells (a condition called by Roux "framboisea"). This condition (also seen in fish embryos) occurs after the frog's embryo has partially regained its semipermeability, and may be due to an abnormal increase in permeability by the salt solution.

J. F. McClendon
Physiological Laboratory,
Medical School,
University of Minnesota,
June 1, 1914

---

[10] Although it is more permeable to water than to salts.

THE AMERICAN CHEMICAL SOCIETY. III

DIVISION OF PHYSICAL AND INORGANIC CHEMISTRY

G. A. Hulett, Chairman
R. C. Wells, Secretary

Rapid Detection of Arsenic in Poison Cases by the Marsh Test: James R. Withrow.

It seems to have been the experience for a long time that the number of cases where arsenic is the poison used exceeds that of all other poisons combined. Certain and rapid detection is therefore a matter of much moment. Any effort to make old methods more certain and to eliminate possibility of error by contamination or to abbreviate, thus reducing opportunity for loss, are desirable. The Berzelius-Liebig modification of the Marsh test (1836) has long enjoyed confidence as one of most satisfactory tests. It requires for universal certainty of results the elimination of organic matter. This is slow, tedious and furnishes much opportunity for loss or contamination. The Reinsch test (1841) is rapid and simple, using the minimum of added reagents. In its present form its results are uncertain and seldom removed from the region of doubt. It does not require the preliminary removal of organic matter. The present work is believed to have made the detection of arsenic much more certain by eliminating entirely the destruction of organic matter. The arsenic is secured on copper strips as in the usual Reinsch procedure. These strips are introduced into a "duplex" Marsh apparatus which has been devised in this work. By the "duplex" feature (two hydrogen generators) no arsenic is lost while displacing air from the generator containing the copper strips which possibly contain arsenic. The use of two generators can be dispensed with by introducing an extra reagent to dissolve the arsenic from the copper. Either procedure greatly reduces the time necessary for the detection of arsenic with all the precision of Marsh's method. The new procedure has already been tried with thorough satisfaction in two poisoning cases where the presence of arsenic was proven finally to be present by the older procedures. The new procedure consumes but an hour or two where the old ones consumed usually one or more days.

The Decomposition Voltages of Salts in Liquid Ammonia. I. The Ammonium Salts: H. P. CADY AND C. A. NASH.

Adsorption and Stabilization: J. C. BLUCHER AND E. F. FARNAU.

Further experimental facts are adduced to substantiate Bancroft's stabilization theory of dyeing. These include examples of adsorption of dyestuffs and inorganic compounds on colloidal hydrous aluminium-, copper- and cobalt-oxides.

The Ideal Diffusion Coefficient and a New Fundamental Law of Diffusion: G. MCP. SMITH.

Further Observations on the Preparation of Selenic Acid and Selenates: PHILIP L. BLUMENTHAL.

A Burette Calibrating Pipette: E. C. FOULK.

Preparation of a Standard Magnesium Salt Solution: E. C. FOULK AND O. R. SWEENEY.

Concerning the Atomic Weights of Carbon and Sulphur: THEODORE W. RICHARDS AND C. R. HOOVER.

In order to verify the silver-halogen standard of atomic weights by reference to a ratio entirely different, a precise quantitative comparison was made between sodium carbonate and silver. The purest sodium carbonate was fused in a stream of carbon dioxide. It was then with all possible care analyzed exactly with very pure hydrobromic acid, and the amount of silver needed to precipitate the bromine was determined as well as the weight of silver bromide. For every 10.59950 grams of sodium carbonate 21.5760 grams of silver were needed. Hence carbon according to the International Standard of Atomic Weights became 12.005, sodium being 22.995. If silver is taken as 107.871, carbon became exactly 12. These results are completely concordant with the usually accepted values concerning carbon and silver. The agreement is striking and affords a much-needed and very welcome confirmation of the whole fabric of our table of atomic weights. The investigation was continued by converting weighed amounts of the purest sodium carbonate into sodium sulphate. The results were concordant among themselves, but pointed to a somewhat smaller atomic weight of sulphur than that usually recognized, namely, 32.055, if silver is taken as 107.88. This research verifies in a striking way that published by one of the authors, twenty-four years ago. The technique of this work will be of great value to any one desiring to make exact acidimetric or alkalimetric analyses.

The Critical Point and the Significance of the Quantity b in the Equation of van der Waals: THEODORE W. RICHARDS.

In this paper many results (especially those of Kamerlingh-Onnes) were quoted to show that the apparent bulk of the molecules of gases must be supposed to change according to circumstances. It was pointed out that the magnitude and direction of this change is such as would be expected if the molecules and atoms are compressible, but, if this is the case, the reasoning of van der Waals, which infers that the bulk of the molecules is only one quarter of b, is no longer sound, for this reasoning assumes the incompressibility of the molecules. The present argument shows rather that the actual bulk of the molecules when uncompressed by collision or by the compressing effect of affinity must be much larger than has been supposed, indeed larger than the actual bulk of the liquid under ordinary conditions, and perhaps that assumed at the critical point. It was pointed out that the continuity between the liquid and the gaseous states may be supposed to exist, if at all, only at the critical point, and that the application of the equation of van der Waals to liquids is of doubtful significance. The critical temperature is defined by supposing that it is the point where the kinetic vibrational energy of the molecules is just barely enough to separate them when the outside pressure (added to their own affinity) is just sufficient to bring, on the average, the molecular surfaces into contact. In conclusion, it is clear that this interpretation of these facts is in complete accord with the theory of compressible atoms. Indeed, the various phenomena concerned seemed to be thus explained better than in any other way.

The Present Status of the Absolute Standard of Pressure: Theodore W. Richards.

The object of this paper was to point out the fact that the absolute or C. G. S. standard of pressure is being more and more used by those actually having to do with the pressure-measurement. Various meteorologists, chemists, physicists and engineers are using it regularly; the United States Weather Bureau, the Blue Hill Observatory, and the Weather Office in England are adopting it as their method of recording atmospheric pressures for scientific study. There is still some conflict in nomenclature, but it is to be hoped that the proposal adopted by the International Congress of Physicists, at Paris, in 1900, and independently suggested by the writer, that the "absolute atmosphere" (or the pressure of a megadyne per square centimeter) should be called the "megabar" or "megabarie," will be generally adopted. This "absolute atmosphere" is 1.3 per cent. less than the old atmosphere, and is the pressure exerted by a column of mercury 750.1 centimeters high at 45° latitude and 0° Centigrade.

A Method for Producing a Reproducible Contact Potential between Liquids: E. P. Schoch.

The Relation between the Concentrations and the Potential of the Ferrous-ferric Pole: E. P. Schoch. (Lantern.)

New Electro-analytical Methods for Lead, Tin, Copper and Antimony: E. P. Schoch and D. J. Brown. (Lantern.)

Contribution to the Knowledge of the Actinium Series: Herbert N. McCoy and Edwin D. Leman.

Solutions of Some Formates and of Hydrogen Chloride in Anhydrous Formic Acid-gases of Apparent Agreement of Strong Electrolytes with the Mass Law: H. I. Schlesinger and A. W. Martin.

When the degree of ionization of solutions of sodium, of phenyl-ammonium, of potassium and of ammonium formates in anhydrous formic acid is calculated from the conductivities of these solutions, the values agree very closely with the equilibrium law up to concentrations, varying from 0.3 to 0.55 molar in the several cases. These electrolytes are highly ionized in this solvent, as shown by the ionization constants, which are 0.75, 0.74, 0.95, 1.15 for the salts in the order in which they are named. Hydrogen chloride also agrees with the law; its constant is 0.04. When the conductivities are corrected for the viscosity of the solution the agreement with the law is not found.

Vapor Tensions in Alcoholic Solutions: O. F. Tower and A. F. O. Germann.

This is a continuation of the work published in the *Journal* of the society, 1908, p. 1219. Vapor pressures were measured exactly as described in that paper by means of the Morley gauge. The new feature is the preparation of the solutions entirely out of contact with air. Methyl and ethyl alcohols were used as solvents, and, after being purified and then fractionated *in vacuo,* were distilled directly on to the solute. Potassium iodide, lithium chloride, benzil and tetramethylammonium iodide were the solutes employed. Curves drawn with the concentrations as abscissas and the lowering of the vapor tension as ordinates are fairly regular, those of the salts rising more rapidly with the increase in concentration than those of the organic solutes. The molecular weights of the latter, as calculated, are approximately normal, while those of the salts are about one half the formula value and do not vary much with the concentration. The work is being continued to see whether this last statement is confirmed by further experiments.

Arsenious Oxide as a Starting Material in Acidimetry: Alan W. C. Menzies and F. N. McCarthy.

Equilibria in the Systems, Water, Acetone and Inorganic Salts: Geo. B. Frankforter and Lillian Cohen.

An investigation is made of the isotherms at 20° of the systems, water, acetone salts. The salts used are KF, K_2CO_3, $CaCl_2$ and NaCl. The comparative efficiency of these salts in "salting" out acetone from an aqueous solution is determined. KF is the most and NaCl is the least efficient. The amount of acetone present in an aqueous solution can be determined by the formation of layers when the potassium fluoride is added to the solution. Within certain limits methyl alcohol acts as if it were water and will not interfere in this determination.

The Colorimetric Determination of Manganese by Means of Periodate: H. H. WILLARD AND L. H. GREATHOUSE.

The solution of manganese salt containing excess of nitric, sulfuric or phosphoric acid is boiled for a minute after addition of potassium periodate. The manganese is oxidized to permanganic acid, the periodic acid being reduced to iodic acid. Small amounts of hydrochloric acid are without influence, being quickly oxidized to chlorine. The concentration of acid above a certain minimum may be varied within wide limits. In the presence of iron, sulfuric or phosphoric acid must be present to prevent the precipitation of ferric periodate. By means of a colorimeter, the solution is compared with a standard similarly prepared.

Electromotive Behavior of Soluble Sulfides: R. C. WELLS.

From a study of the potentials shown by various solutions of sulfides with a platinum electrode it was concluded that the electromotive behavior of the polysulfides depends on the relative proportions of the sulfides present, but that in acid solutions where free sulfur is apparently the only oxidation product of sulfide ions the potential of solutions which are very slightly oxidized can be expressed by the equation

$$E = -0.26 - 0.029 \log[s^{--}],$$

since the concentration of the free sulfur is constant and equal to its solubility in water.

The Phase-rule Investigation of Addition Reactions: JAMES KENDALL.

The freezing-point modes of the two-component system dimethylpyrone-acid have been examined for a large number of organic acids and phenole. The existence of thirty-seven addition compounds has been demonstrated. The results obtained are discussed in their bearing on the constitution of dimethylpyrone and the quadrivalence of oxygen. The reaction is considered to be ionic, and the compounds formed to be true oxonium salts. The method is generally applicable to the study of organic addition reactions.

Peculiar Action of Iodine: CHARLES T. P. FENNEL.

Distribution of Caffeine and Antipyrin Between Chloroform and Aqueous Solutions: W. O. EMERY AND C. D. WRIGHT.

Reaction in Non-aqueous Solvents: O. L. BARNEBEY.

Separation of Potassium from Sodium by Extraction of their Chlorplatinates with Acetone: O. L. BARNEBEY.

Some Compounds Belonging to the Ammonia System of Acids, Bases and Salts: E. C. FRANKLIN.

(1) *The Action of Potassium Amide on the Amides of Silver, Barium, Strontium, Calcium, Lithium and Sodium.* By Edward C. Franklin. It will be recalled that the writer and his collaborators have prepared compounds of the formulas,

$Sn(NK)_2 \cdot 4NH_3$, $Zn(NHK)_2 \cdot 2NH_3$, $PbNK \cdot 2\frac{1}{2}NH_3$ and

$$N \equiv Ti - NHK,$$

to which, in view of the analogy existing between these compounds as derivatives of ammonia on the one hand, and the stannate, zincate, plumbite and titanate of potassium as derivatives of water on the other, have been given the respective names, potassium ammonostannate, potassium ammonozincate, potassium ammonoplumbite and potassium ammonotitanate. Furthermore it will be remembered that similar ammono salts containing thallium and magnesium have been prepared, an accomplishment which is noteworthy in view of the fact that the corresponding aquo salts are unknown. It now appears that not only are the above-mentioned salts formed in a manner similar to that used in the preparation of potassium ammonozincate but that also the amides of silver, barium, strontium, calcium and even lithium and sodium enter into reaction with potassium amide in solution in liquid ammonia to form sharply defined products of the respective formulas,

$$AgNHK \cdot NH_3,\ BaNK \cdot 2NH_3,\ SrNK \cdot 2NH_3,$$

$CaNK \cdot 2NH_3$, $LiNK_2 \cdot 2NH_3$ and $NaNK_2 \cdot 2NH_3$. If the compound, $Zn(NHK)_2 \cdot 2NH_3$, is properly designated as potassium ammonozincate, and it certainly is if the compound $Zn(ONa)_2 \times H_2O$, is called potassium (aquo) zincate, then these new compounds must receive the respective names, monopotassium ammonoargentate, monopotassium ammonobarate, monopotassium ammonostrontiumate or strontianate, monopotassium ammonocalciumate or calcate, dipotassium ammonolithiumate (or possibly lithianate) and dipotassium ammonosodiumate (or sodate or natronate). This procedure is of course pushing analogy to the limit and it may be that these products are not salts at all, but are molecular compounds as represented by the formulas

$$AgNH_2 \cdot KNH_2,\ Ba(NH_2)_2 \cdot 2KNH_2,$$
$$NaNH_2 \cdot 2KNH_2,$$

etc., whatever the significance of such formulas may be. The writer hopes, by transference measurements, to be fortunate enough to determine whether or not such a substance as $NaNK_2 \cdot 2NH_3$, for example, in solution in liquid ammonia dissociates into NaN anions and K cations, though it may well turn out that such experiments will show no results because of ammonolytic decomposition of the salt, for certainly if acid at all sodium amide must be a very weak one.

(2) *The Action of Potassium Amide on Cadmium, Nickel and Chromium Salts in Liquid Ammonia Solution.* By E. C. Franklin and George S. Bohart. Experience in this laboratory has shown that metallic amides, imides or nitrides are precipitated when a liquid ammonia solution of the ammono base, potassium amide, is added to similar solutions of the salts of heavy metals. It has also been found when the precipitant is added in excess that, in many cases, compounds are formed which are related to ammonia as the zincates and aluminates are related to water. (*Cf.* preceding abstract.) Following the procedure thus indicated the amides of cadmium and nickel, $Cd(NH_2)_2$ and $Ni(NH_2)_2$, have been prepared, both of which may be deammonated and thus converted into the corresponding nitrides, Cd_3N_2 and Ni_3N_2. It has also been shown that compounds of the second class indicated above are formed when potassium amide is added in excess to solutions of the sulfocyanates of cadmium, nickel and chromium. The products obtained have the composition represented by the empirical formulas, $CdN_4H_8K_2$, $Ni_2N_9H_{18}K_5$ and $Cr_2N_8H_{15}K_3$. Some light is thrown upon the nature of these compounds if they are formulated as follows:

$$Cd(NHK)_2 \cdot 2NH_3, \text{ or } Cd(NH_2)_2 \cdot 2KNH_2,$$

$$K_2NNi{-}NK{-}NiNK_2 \cdot 6NH_3$$

or

$$2Ni(NH_2)_2 \cdot 5KNH_2,$$

and

$$KN{=}Cr{-}NK{-}Cr{=}NK \cdot 5NH_3$$

or

$$(NH_2)_2Cr{-}NH{-}Cr(NH_2) \cdot 3KNH_2.$$

They may receive the respective names; potassium ammonocadmiate (or cadmate), potassium ammononickelate and potassium ammonochromate. When potassium nickel cyanide is treated with potassium amide one of the three complex compounds of the respective formulas,

$$Ni_3N_2H_2K_4(CN)_6 \cdot 8NH_3$$

(which loses ammonia to form $Ni_3N_2H_2K_4(CN)6_2$), $NiNHK_2(CN)_2$ and $Ni_3N_{11}H_{22}K_7(CN)_2$, is formed depending upon the relative quantities of the nickel salt and potassium amide used. We are unable to assign rational formulas to these compounds. Formulation as follows, however, furnishes some clue to their nature.

$$(1) \quad K_2(CN)_3Ni{-}NH{-}Ni{-}NH{-}Ni(CN)_3 \\ K_2 \cdot 8NH_3$$

or

$$K_4Ni(CN)_6 \cdot 6NH_3 \cdot 2Ni(NH_2)_2.$$

$$(2) \quad K(CN)_2NiNHK$$

or

$$K_2Ni(CN)_4 \cdot Ni(NHK)_2.$$

$$(3) \quad (CN)Ni{-}NK{-}Ni{-}NK{-}Ni \\ (CN) \cdot 5KNH_2 \cdot 4NH_3.$$

Number 1 is a mixed potassium nickel cyanide-nickel amide or imide. Number 2 is a mixed potassium nickel cyanide-potassium ammononickelate, as is also number 3.

Gas Analyses by Liquefaction and Fractionatives and the Condition of Natural Gas in the Earth's Strata: G. A. Burrell and Frank M. Seibert.

The exact composition of natural gas such as is used in Pittsburgh, Pa., Cincinnati, Ohio, and many other cities is shown for the first time. As a result of this work it is shown that these gases are accumulated in their deposits in the gaseous condition, and not as liquids. If present therein as liquids it would be possible for single small subterranean reservoirs to hold much larger quantities of gas than they now do.

The Condition of Natural Gas in the Earth's Strata: G. A. Burrell and Frank M. Seibert. (Lantern.)

Collisional and Diffusional Viscosities: Eugene C. Bingham.

Heat and Chemical Energy of Molecules, Atoms and Subatoms: J. E. Siebel.

Electrostenolysis: Harry N. Holmes.

By electrostenolysis is meant the deposition of a metal or its oxide in very fine capillaries when the solution filling these capillaries is electrolyzed. Braun and Coehn experimented only with cracks in glass tubes. The author improved this method by the use of capillary membranes in the form of glass tubes packed with finely powdered substances such as glass, sulfur and silica. This multiplies greatly the capillary surfaces and permits the use of many different membranes. Working with tubes so prepared, the author added a number of examples of electrostenolysis to the list recorded by Braun.

Charles L. Parsons,
Secretary

(*To be concluded*)