Ephraim calls attention to what he considers to be a fundamental distinction between the hydrates and the ammonates, namely that the vapor-pressure curves of the hydrates show transition and inversion points, while those of the ammonates do not. He also states that while the hydrates have definit fields of existence, the ammonates have not, and explains this on the supposition that saturated solutions of the ammonates are not formed. All of these conclusions concerning the ammonates are in direct contradiction with the classical researches of Roozeboom[1] upon the system NH_4Br, NH_3, and with the results obtained in this laboratory during the past three years. As pointed out by Mr. Friedrichs,[2] the ammonates studied by Ephraim happen to be, for the most part, insoluble in liquid ammonia, as shown by the work of Franklin and Kraus.[3] These insoluble ammonates, which indeed under ordinary conditions do not show transition or inversion points, do not have definitly bounded fields of existence, and do not yield saturated solutions, have been compared by Ephraim with soluble hydrates, and an erroneous generalization, covering both soluble and insoluble ammonates, has been formulated.

Summary.

In the present investigation it has been shown:

(1) That ammonium trinitride, unlike ammonium chloride,[4] ammonium bromide,[5] and ammonium iodide,[4] forms a diammonate, with the formula $NH_4N_3.2NH_3$, obtained in the form of clear, colorless, somewhat elongated plates, that appear to be neither regular nor tetragonal.

(2) That the diammonate is stable at —33°, showing a dissociation pressure of about 22.8 cm. at this temperature. It is not stable at 0°, the inversion point being located at about —9°.

(3) That one gram of liquid ammonia will dissolve seven-tenths gram of ammonium trinitride at —33°, and one gram at 0°. The vapor pressure of the saturated solution at these two temperatures is respectively 43.7 and 149 cm.

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STUDIES ON OSMOSIS.

By C. Ferdinand Nelson.

Received April 1, 1913.

Introduction.

The exact nature of osmosis and of osmotic phenomena has engaged the attention of scientists for over a century. During this time many

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[1] *Rec. trav. chim.*, 4, 361 (1885); *Z. physik. Chem.*, 2, 460 (1888).

[2] "Ueber die Natur der Nebenvalenzen. Bemerkungen zur Abhandlung des Herrn Fritz Ephraim." *Z. physik. Chem.*, 82, (1913).

[3] *Am. Chem. J.*, 20, 820–36 (1898).

[4] Troost, *Compt. rend.*, 88, 578 (1879).

[5] Troost, *Ibid.*, 92, 715 (1881); Roozeboom, *loc. cit.*

theories have been advanced to explain the process as a whole as well as the particular role played by the various factors involved, *viz.*, the solvent, the solute, and the intervening membrane. So much, however, has recently been written concerning both the history and the theory of this subject that it will be sufficient in this connection merely to call attention to a few of the views which have been advanced at various times and which find greater or less acceptance to-day.

According to what might be called the "sieve" theory of osmosis, the osmotic membrane acts by allowing the molecules of the solvent to pass through the membrane while the molecules of the solute remain behind. Osmotic pressure is assumed to be due to a bombardment of the molecules of the solute against a membrane which is not permeable to them. The tendency of the solute to expand into a larger space causes the molecules of the solvent to pass through the membrane and into the space occupied by the solute until an equilibrium is established. The membrane acts in a purely mechanical manner holding back the molecules of the solute and allowing those of the solvent to pass through.

The "surface tension" theory of osmosis assumes osmotic effects to be due to the differences in surface tension existing between solvent, solute, and intervening membrane. According to this view osmosis becomes purely a capillary phenomenon. Among those favoring this view we may mention Traube,[1] Batelli and Stephanini,[2] and Bigelow.[3]

The chemical or "selective" theory of osmosis, the first clear statement of which we owe to Kahlenberg,[4] assumes osmosis to be a selective phenomenon depending on the specific natures of the solvent, solute, and intervening membrane. Kahlenberg[5] sums up his researches on this subject by saying: "Whether osmosis will take place in a given case or not depends on the specific nature of the septum and the liquids that bathe it, and if osmosis does occur, these factors also determine the direction of the main current and the magnitude of the pressure developed."

This view of the nature of osmosis carries with it the assumption of a labil compound formed between the membrane and the solvent on the one hand, and between the solvent and the solute on the other, and ascribes the movement of liquid into the osmotic cell by assuming that the solute robs the membrane of its imbibed solvent, the membrane in turn imbibing more solvent which is again extracted by the solute, this process

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[1] *Pflüger Archiv.*, **123**, 419 (1908); *Phil. Mag.*, **6**, 8, 704 (1904); *Zeit. Phys. Chem.*, **105**, 541 (1904); *Chem. Zeitschrift*, **26**, 1071 (1902); *Ber. Chem. Ges. Berlin*, **31**, 160 (1898); *Anal. Chem. Phys.*, **62**, II, 490 (1897); *Zeit. Anorg. Chem.*, **8**, 323 (1895).

[2] *Atti R. Accad. Lincei*, [5] 14, II, 3 (1905); [5] 16, I, 11 (1907).

[3] THIS JOURNAL, **29**, 1675 (1907); **31**, 1194 (1909).

[4] *Trans. Wis. Acad. Sci.*, **15**, 209 (1906); *Jour. Phys. Chem.*, 10, 141 (1906).

[5] *Loc. cit.*

being repeated until equilibrium is established. Experiments in osmosis thus become distribution experiments.

In the article just referred to, Kahlenberg measured the direct osmotic pressures of pyridine solutions of lithium chloride, cane sugar, and silver nitrate when solutions of these substances in pyridine were separated from pure pyridine by a rubber membrane. A little later, W. G. Wilcox[1] measured the direct osmotic pressures of the same substances in extremely dilute solutions. Both found that their results varied widely from those calculated according to the gas laws, or "that the gas laws do not hold for the cases tried." To extend this work still further it first became necessary to find additional substances soluble in pyridine and suitable for direct osmotic-pressure measurements and this was accordingly first undertaken.

Solubility Determinations.

A list of some of the substances examined to determin whether they were soluble in pyridine has been added, more to emphasize and illustrate the very important point that solubility is a specific phenomenon which depends on each individual solvent and solute and can be determined only by actual trial, than to present additional data on solubility. The determinations recorded were only roughly made and are not to be considered in any sense as quantitative. The word "insoluble" as here used means that at best only traces went into solution. Those designated as "soluble" vary from one % up to being consolute with the solvent. Substances marked "slightly soluble" run in fractions of a %.

SOLUBILITY TABLE.—SOLVENT PYRIDINE.

Dextrose	soluble	Cholesterin	soluble
Levulose	soluble	Bile salts	soluble
D-Fructose	soluble	Urea	slightly soluble
Mannite	soluble	Silver chloride	slightly soluble
Galactose	slightly soluble	Silver bromide	soluble
Lactose	slightly soluble	Silver sulfocyanide	soluble
Glycogen	insoluble	Silver cyanide	soluble
Inulin	insoluble	Silver acetate	soluble
Dextrin	insoluble	Silver nitrate	soluble
Starch	insoluble	Silver sulfate	slightly soluble
Thymol	soluble	Silver citrate	insoluble
Phenol	soluble	Silver tartrate	insoluble
Resorcin	soluble	Silver iodide	insoluble
Camphor	soluble	Lead chloride	slightly soluble
Camphor monobrom	soluble	Lead nitrate	soluble
Hexamethyleneamine	soluble	Lead acetate	soluble
Acetanilid	soluble	Lead bromide	slightly soluble
Chloral hydrate	soluble	Lead abietate	soluble
Saccharin	soluble	Lead sulfocyanide	soluble
Cocoa butter	soluble	Lead cyanide	insoluble

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[1] *Jour. Phys. Chem.*, 14, 576 (1910).

Solubility Table (*continued*).

Lead iodide	insoluble
Lead iodate	insoluble
Lead chromate (basic)	insoluble
Lead tartrate	insoluble
Lead bromate	insoluble
Lead sulfate	insoluble
Lead chromate	insoluble
Albumin	insoluble
Mucin	insoluble
Edestin (hemp)	insoluble
Casein (milk)	insoluble
Globulin (brazil nut)	insoluble
Vitellin (egg yolk)	insoluble
Gelatin (connec. tissue)	insoluble
Cerebrin	insoluble
Egg anti-albumin	insoluble
Nucleo-albumin (pancreas)	insoluble
Peptone	insoluble
Creatin	insoluble
Creatinin zinc chloride	insoluble
Hypoxanthine silver chloride (from muscle)	insoluble
Leucin	insoluble
Uric acid	insoluble
Glycocoll	insoluble
Oleic acid	soluble
Palmitic acid	soluble
Stearic acid	soluble
Boric acid	soluble
Hippuric acid	soluble
Tartaric acid	soluble
Benzoic acid	soluble
Salicylic acid	soluble
Malic acid	soluble
Cholic acid	soluble
Citric H_2O	soluble
Strychnine (alkaloid)	soluble
Strychnine sulfate	slightly soluble
Morphine hydrochloride	soluble
Morphine sulfate	soluble
Copper chloride (ous)	soluble
Copper bromide	soluble
Copper iodide	soluble
Copper acetate	soluble
Copper abietate	soluble
Copper oleate	soluble
Copper palmitate	soluble
Copper stearate	soluble
Copper nitrate	slightly soluble
Copper potass. chloride.	slightly soluble
Copper sulfate $5H_2O$	insoluble
Copper carbonate	insoluble
Copper ammon. sulfate	insoluble
Copper arsenite	insoluble
Copper arsenate	insoluble
Copper aluminate	insoluble
Lithium carbonate	practically insoluble
Lithium salicylate	soluble

Permeability of Pyridine Solutions of Various Salts when Separated from Pure Pyridine by a Rubber Membrane.

Maximum osmotic-pressure values have not been attempted in the following experiments although the exact rise, in centimeters of liquid, within the osmometer tube, has been carefully observed and recorded in nearly every case. No systematic attempt at stirring the outer and inner liquids has been made, neither has evaporation of solvent and solute been absolutely prevented. Special effort has, however, been made to keep the conditions under which one experiment was performed exactly like those of all the others so that conclusions from comparative values might be drawn.

The following experiments were made with the object of determining first whether the particular compound under consideration passed through the membrane used, *i. e.*, whether the membrane was so-called "semipermeable" toward the particular solute. This was done, as mentioned before, in the hope of finding additional substances suitable for measuring direct osmotic pressures in pyridine solutions, using rubber as the septum. In the second place, to determin by a study of the nature and kinds of the compounds that pass through the membrane as well as those that remain behind whether the process of osmosis is essentially physical or chemical in nature.

Apparatus and Chemicals.

The osmometers used were similar to the ones used and described by Kahlenberg[1] in his osmotic investigations. A thistle tube having a forty-five degree flare at its wide end was selected. Over this the rubber membrane used was carefully stretched so that every part was taut and free from wrinkles. A large number of windings with strong cotton thread was found to make the joint between the glass and the rubber perfectly tight. Before beginning each experiment the osmometer used was carefully tested for any possible leaks by immersing it in dry pyridine and putting the inner membrane under pressure. The smallest leak will be readily detected by the appearance of air bubbles in the liquid. After making sure that the osmometer was perfectly tight it was filled by means of a small funnel and suspended in the outer liquid contained in a tall beaker but slightly larger than the osmometer.

In the following experiments, unless otherwise specifically mentioned, the membrane used was very fine "dental" sheet rubber. The liquid within the osmometer will be spoken of as the inner liquid, that on the outside of the osmometer as the outer liquid. The outer liquid unless otherwise mentioned was carefully dried pyridine. The rise of liquid within the osmometer tube is recorded in centimeters of liquid. Pressures above 21 cm. are not recorded since at this point the contents of the tube overflowed. The temperature of the room where the experiments were carried on was kept automatically at 70° F.

All of the materials used were the very best obtainable. The chemicals were either of Merck's or Schuchardt's make. In all cases where any considerable pressure was developed particular care was exercised to remove moisture. The salts were carefully powdered and dried over sulfuric acid for days. The pyridine used was made by Merck (labeled Merck's medicinal). It was kept over fused caustic potash for weeks before being used. To guard the main stock as much as possible from becoming contaminated with moisture, that needed for daily use was kept in a small bottle also over fused caustic potash. A number of the physiological compounds used have been kindly furnished by Dr. H. C. Bradley. The abietates and stearates used were prepared and furnished by Dr. E. O. Ellingson and Mr. F. C. Evans.

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[1] *Loc. cit.*

TABLE I.—SEPTUM RUBBER.

Expt. No.	Inner liquid.	Observation.
1	5% solution of calcium abietate in pyridine.	No rise of liquid in the osmometer after standing for 6 days. Outer liquid contained an amount of the solute.
2	5% solution of strontium abietate in pyridine.	Membrane broken.
3	5% solution of chromium abietate in pyridine.	Slight decrease during the first 24 hours. No further rise or fall during the next 6 days. Solute had gone through the membrane in considerable quantity.
4	5% solution of zinc abietate in pyridine.	1 cm. rise in osmometer tube after standing for 6 days. Considerable solute had passed through the membrane and into the outer liquid.
5	5% solution of manganese abietate in pyridine.	No rise within the osmometer tube after standing for 6 days. Solute was found in the outer liquid in considerable quantity.
6	5% solution of iron abietate in pyridine.	No rise of liquid within the osmometer tube after standing for 6 days. Solute was found in the outer liquid.
7	5% solution of nickel abietate in pyridine.	A rise of 2 cm. was observed during the first 24 hours. On the 6th day the liquid within the osmometer tube reached its maximum of 5 cm. Outer liquid contained solute.
8	5% solution of cobalt abietate in pyridine.	A rise of 2.5 cm. during the first 24 hours. Maximum rise of 10 cm. on the 6th day. The solute was found in the outer liquid.
9	5% solution of cadmium abietate in pyridine.	1 cm. rise during the first 24 hours. No further change during the next 5 days. The solute was found in the outer liquid.
10	Concentrated solution of copper abietate in pyridine.	No rise was observed after standing for 6 days. The solute was found in the outer liquid.
11	Concentrated solution of silver abietate in pyridine.	A maximum rise of 2.5 cm. on the 6th day. The solute was found in the outer liquid.

TABLE II.

Expt. No.	Inner liquid.	Observation.
1	Saturated solution of copper stearate in pyridine.	No rise of liquid within the osmometer tube during the 11 days that the experiment was running. Outer liquid contained a considerable quantity of solute.
2	Saturated solution of cadmium stearate in pyridine.	A slight rise during the first 24 hours (less than a cm.). No further change during the 14 days that the experiment was running. Outer liquid contained a considerable quantity of the solute.
3	Saturated solution of manganese stearate in pyridine.	Very slight increase during the first 24 hours. No further change during the 14 days that the experiment was running. Outer liquid contained a considerable quantity of solute.
4	Saturated solution of cobalt stearate in pyridine.	No appreciable rise of liquid within the osmometer tube during the 14 days that the experiment was running. Outer liquid contained a considerable quantity of the solute.
5	Saturated solution of nickel stearate in pyridine.	No rise of liquid within the osmometer tube during the 14 days that the experiment was running. Outer liquid contained considerable amount of solute.
6	Saturated solution of copper oleate in pyridine.	A rise of 1 cm. during the 7 days that the experiment was running. Outer liquid contained considerable quantity of solute.
7	Saturated solution of lead oleate in pyridine.	No rise of liquid within the osmometer tube during the 12 days that the experiment was running. Outer liquid contained a considerable quantity of the solute.
8	Concentrated solution of copper palmitate in pyridine.	No rise of liquid within the osmometer tube was observed during the 11 days that the experiment was running. Outer liquid contained considerable amount of solute.

TABLE III.

Expt. No.	Inner liquid.	Observation.
1	A tenth molar solution of phenol in pyridine.	No rise of liquid within the osmometer tube during the 16 days that the experiment was running. Outer liquid contained a considerable quantity of phenol.

TABLE III (*continued*).

Expt. No.	Inner liquid.	Observation.
2	10% solution of thymol in pyridine.	No rise of liquid within the osmometer tube during the 15 days that the experiment was running. (A slight decrease took place.) Outer liquid contained thymol.
3	Saturated solution of copper formate in pyridine.	A rise of 10 cm. was developed during the first 24 hours. No further rise occurred. Outer liquid contained some of the solute.
4	Saturated solution of cuprous iodide in pyridine.	No rise of liquid was observed during the 11 days that the experiment was running. The solute had gone through the membrane and into the outer liquid.
5	Concentrated solution of silver cyanide in pyridine.	A rise of 2.5 cm. developed during the first 24 hours. On the 5th day a maximum rise of 10 cm. was developed (expt: was run for 26 days). An accident prevented the testing of the outer liquid.
6	Saturated solution of cuprous chloride in pyridine.	A maximum rise of 15 cm. was developed during the 12 days that the experiment was running. Outer liquid contained a considerable quantity of the solute.

TABLE IV.

Expt. No.	Inner liquid.	Observation.
1	Saturated solution of hippuric acid in pyridine.	Osmometer tube full (21 cm.) on the 3rd day. Some of the solute had gone through the membrane.
2	Saturated solution of dextrose in pyridine	Osmometer tube full on the 3rd day. Some dextrose was found in the outer liquid.
3	A tenth molar solution of dextrose in pyridine.	Maximum rise of 19 cm. on the 2nd day. Some dextrose was found in the outer liquid.
4	Saturated solution of levulose in pyridine.	A rise of 18 cm. was developed during the first 6 hours. The next morning the tube had overflown. Some of the solute had gone through the membrane.

TABLE IV (*continued*).

Expt. No.	Inner liquid.	Observation.
5	Saturated solution of silver sulfocyanide in pyridine.	The liquid within the osmometer tube overflowed during the first 24 hours. Outer liquid contained some of the solute.
6	Saturated solution of lead nitrate in pyridine.	Osmometer tube was filled during the first 24 hours (21 cm.). Some of the solute had passed through the membrane. The major current was, however, decidedly in the other direction.
7	A tenth molar solution of lead nitrate in pyridine.	Maximum rise of 14 cm. on the 2nd day. Comparatively small amounts of solute went through the membrane.

Effect of Adding Water in Various Amounts to the Inner and Outer Liquids.

Four series of five experiments each were made to determin the effect of adding water in various amounts—first to the outer and inner liquids separately; then simultaneously. One control experiment was run in each case. Enough solution was made in each instance to serve for the whole series so that there could be no question as to changes in concentration. The water, whenever added, was measured in drops to measured amounts of outer and inner liquids. Table IX shows the effect of adding large quantities of water to inner and outer liquids.

TABLE V.

Inner liquid.	Outer liquid.	Observation.
1. A tenth molar solution of cane sugar in pyridine.	Pyridine (carefully dried).	Maximum rise of 18 cm. on the second day.
2. A tenth molar solution of cane sugar in pyridine. To 20 cc. of outer and inner liquids, 2 drops of water were added.	Pyridine (carefully dried).	Liquid within osmometer tube reached a height of 21 cm. and overflowed on the 3rd day.
3. Inner and outer liquids same as in Experiment 1. To 20 cc. of outer and inner liquids, 15 drops of water were added.		Maximum rise of 11 cm. on the second day.
4. Inner and outer liquids as above. 15 drops of water were added to the inner liquid only.		Liquid within the tube overflowed on the 4th day.
5. Inner and outer liquids as above. 15 drops of water were added to the outer liquid only.		A decrease of about 8 cm. of liquid was noted which remained for 8 days after which the liquid slowly rose. On the 14th day the liquid within the osmometer was 3 cm. above the original mark.

TABLE VI.

Liquids.	Observation.
1. Inner liquid: A tenth molar solution of silver nitrate in pyridine. Outer liquid: Carefully dried pyridine.	Maximum rise of 16.5 cm. on the 4th day. (13.5 cm. on the 2nd day.)
2. Inner and outer liquids as above. To 20 cc. of outer and inner liquids, 2 drops of water were added.	Maximum rise of 19 cm. on the 2nd day.
3. Inner and outer liquids as above. To 20 cc. of outer and inner liquids 15 drops of water were added.	Maximum rise of 8 cm. on the 2nd day.
4. Inner and outer liquids as above. 15 drops of water were added to the inner liquid only.	Liquid almost filled osmometer tube (20 cm.) during the first 16 hours. Overflowed a little later.
5. Inner and outer liquids as above. 15 drops of water were added to the outer liquid only.	A decrease of about 10 cm. of liquid took place during the first 24 hours. This was maintained for 5 days when the liquid began to rise until on the 7th day it had filled the osmometer tube (21 cm.).

TABLE VII.

Inner liquid.	Outer liquid.	Observation.
1. A tenth molar solution of lithium chloride in pyridine.	Carefully dried pyridine.	A maximum rise of 20 cm. on the 6th day.
2. A tenth molar solution of lithium chloride in pyridine. To 20 cc. of outer and inner liquids, 2 drops of water were added.	Carefully dried pyridine.	Tube full on the 3rd day (21 cm.).
3. A tenth molar solution of lithium chloride in pyridine. To 20 cc. of outer and inner liquids, 15 drops of water were added.	Carefully dried pyridine.	Maximum rise of 19 cm. on 2nd day.
4. A tenth molar solution of lithium chloride in pyridine. 15 drops of water were added to inner liquid only.	Carefully dried pyridine.	Tube overflowed during first 24 hours.
5. A tenth molar solution of lithium chloride in pyridine. 15 drops of water were added to outer liquid only.	Carefully dried pyridine.	Decrease of 20 cm. on the 4th day Liquid nearly back to its original mark on the 15th day.

TABLE VIII.

	Inner liquid.	Outer liquid.	Observation.
1.	A tenth molar solution of dextrose in pyridine.	Carefully dried pyridine.	Osmometer tube full on 2nd day.
2.	A tenth molar solution of dextrose in pyridine. To 20 cc. of outer and inner liquids, 2 drops of water were added.	Carefully dried pyridine.	Maximum rise of 20 cm. on the 4th day.
3.	A tenth molar solution of dextrose in pyridine. To 20 cc. of outer and inner liquids, 15 drops of water were added.	Carefully dried pyridine	Maximum rise of 15 cm. on 6th day.
4.	A tenth molar solution of dextrose in pyridine. 15 drops of water were added to the inner liquid only.	Carefully dried pyridine.	Liquid in osmometer tube overflowed during the first 24 hours.
5.	A tenth molar solution of dextrose in pyridine. 15 drops of water were added to the inner liquid only.	Carefully dried pyridine.	Decrease of 21 cm. on the 3rd day. Liquid up to the original mark on the 14th day.

TABLE IX.

	Outer liquid.	Inner liquid.	Observation.
1.	Equal parts of pyridine and water.	Saturated solution of silver sulfate in equal parts of pyridine and water.	Maximum rise of 2.5 cm. during the 18 days that the experiment was running. Traces of silver found in the outer liquid.
2.	Equal parts of pyridine and water.	A tenth molar solution of silver nitrate in equal parts of pyridine and water.	Maximum rise of 1 cm. during the 10 days that the experiment was running.
3.	Equal parts of pyridine and water.	A tenth molar solution of cane sugar in equal parts of pyridine and water.	Rise of less than 1 cm. during the 9 days that the experiment was running.
4.	Equal parts of pyridine and water.	An eighth molar solution of cane sugar in equal parts of pyridine and water.	No rise took place during the 17 days that the experiment was running.
5.	Equal parts of pyridine and water.	A molar solution of dextrose in equal parts of pyridine and water.	No rise took place during the 7 days that the experiment was running.
6.	Equal parts of pyridine and water.	A molar solution of lithium chloride in equal parts of pyridine and water.	No rise took place during the 17 days that the experiment was running.

TABLE IX (*continued*).

Outer liquid.	Inner liquid.	Observation.
7. Equal parts of pyridine and water.	A tenth molar solution of lithium chloride in equal parts of pyridine and water.	Maximum rise of 0.5 cm. within osmometer tube during the 15 days that the experiment was running.
8. Equal parts of pyridine and water.	A tenth molar solution of dextrose in equal parts of pyridine and water.	Maximum rise of 1.5 cm. during the 15 days that the experiment was running.

Discussion of Results.

If the results obtained in the experiments recorded in Table I be examined, it will be seen that, without exception, the abietates of all of the metals investigated pass through the membrane with considerable ease and without producing any considerable rise of liquid within the osmometer tube. The oleates, palmitates, and stearates (Table II) act as do the abietates. Moreover a number of other, widely varying compounds behave in a similar manner. So for instance do pyridine solutions of camphor, phenol, thymol, and benzoic acid (Table III). These compounds appear in the outer liquid in considerable quantity and are all found to be easily soluble in hydrocarbons such as benzene and kerosene; they are, therefore, also soluble in rubber and would pass through such a membrane, as Kahlenberg[1] has previously pointed out.

On the other hand, it has been easy to find a number of compounds, also soluble in pyridine, which, while they pass through the membrane to some extent, do so far less readily and at the same time develop more or less pressure within the osmotic cell, such, for example, are pyridine solutions of silver sulfocyanate, copper chloride, lead nitrate, copper formate, dextrose, levulose, saccharin, and hippuric acid. These compounds do not pass through the membrane so easily nor in so large amounts as those first mentioned and are found to be insoluble or at best only slightly soluble in hydrocarbons.

It seems clear that all of these cases are not fortuitous or in any way exceptional. That they cannot be explained by assuming that osmosis is physical in nature, that capillarity, surface tension, or porosity governs the exchange of solvent and solute through the membrane seems equally evident. It is only by assuming, a chemical attraction and loose chemical combination that these results become at all intelligible.

The mechanism of the formation of such a labil chemical compound between the membrane and the solvent on the one hand, and the solvent and the solute on the other, cannot be conceived of simply as a "solution" of solvent and solute in the membrane where that word merely implies

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[1] *Loc. cit.*

an orderly filling of the membranous interstices or intermolecular spaces by solvent or solute by virtue of capillary attraction. It would be hard to conceive how a slight change in surface tension could hinder or reverse the direction of the main osmotic current to the extent that it actually does. If capillarity here manifests itself, it would be simpler and better to consider it as a physical concomitant of a chemical change rather than as the directing force in producing osmosis.

That, at least in the cases cited, osmosis must be considered as purely chemical in nature is further shown in the experiments in which varying amounts of water were added to the inner and outer liquids separately and simultaneously (Table V to IX). If the results obtained in these experiments be examined, it will be noted that as water is gradually added to both inner and outer liquids there is at first an increased osmotic effect, *i. e.*, the osmotic pressure developed is greater than when only pure solvent is used. As the amount of water is gradually increased the rise of liquid within the osmometer tube progressively decreases until when equal parts of water and solvent are used little or no rise of liquid is observed. Again when water is added only to the inner liquid the invariable result is a flow of solvent into the solute causing the liquid within the osmometer tube to rise rapidly, while if the water be added to the outer liquid there is a preliminary decrease of liquid within the osmometer tube followed by a subsequent rise. Such behavior, it seems, cannot be adequately explained on the basis of porosity or possible changes in surface tension on the part of the membrane or the liquids that bathe it.

Summary and Conclusions.

The direction of the main and minor osmotic currents have been determined for a number of organic and inorganic compounds when pyridine solutions of these compounds have been separated from pure pyridine by a rubber membrane.

The solubility of a number of different compounds in pyridine has been determined.

The effect of adding water in various amounts to the inner and outer liquids of an osmotic cell, to the inner and outer liquids separately and simultaneously, has been determined for a number of different compounds.

Of the compounds examined with the object of determining suitability for use in direct osmotic pressure determinations lead nitrate and dextrose have been found to approximate, most closely, cane sugar and silver nitrate as regards semipermeability towards a rubber membrane using pyridine as solvent.

The results obtained point clearly, at least for the cases investigated, to a chemical basis for osmosis, where chemical selectivity determins the direction of the major and the minor osmotic currents rather than the purely physical factors of porosity, capillarity, and surface tension.

The author desires to take this opportunity to express his obligations and thanks to Professor Louis Kahlenberg under whose direction and guidance the present work was undertaken and prosecuted.

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MADISON, May, 1912.

A NEW METHOD FOR THE PREPARATION OF VANADIUM TETRACHLORIDE.[1]

BY A. T. MERTES.

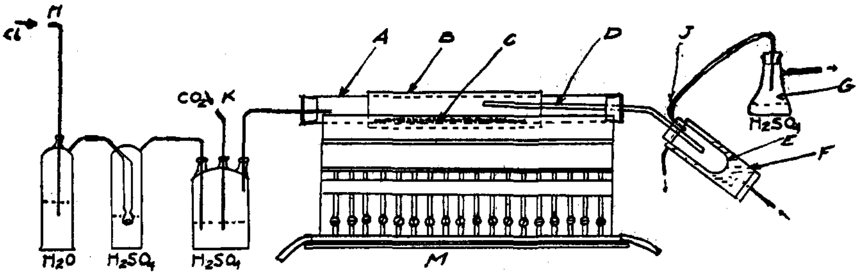
Received March 24, 1913.

The usual methods for the preparation of vanadium tetrachloride involve the fractional distillation and separation of vanadium tetrachloride from a mixture with other chlorides. This fractionation requires time and results in losses, due not only to the imperfect separation of the fractions, but to the inevitable loss of vanadium tetrachloride due to its decomposition.

The writer had occasion to prepare a considerable amount of vanadium tetrachloride and believes the following method to be superior to any given in the reference works or journals. It is essentially the action of chlorine upon ferrovanadium, and takes place as follows:

$$FeV + 7Cl = FeCl_3 + VCl_4.$$

Dry, air-free, chlorine is passed over heated ferro-vanadium contained in a reaction tube. Vanadium tetrachloride distils over while the ferric chloride remains in the tube. The accompanying sketch shows the arrangement of apparatus.



The reaction tube *A*, is made of hard glass about 5 cm. in diameter and about 150 cm. long. A sheet iron jacket, *B*, 8 cm. in diameter, surrounds this tube and leaves an air space of about 1 cm. between it and the glass. This permits of a uniform and slow heating of the tube—the heat being easily regulated by the combustion furnace, *M*. The ferro-vanadium is crushed to about 4 mesh and placed in the reaction tube at *C*. An inclined delivery tube, *D*, extends into the receiver *E*, which is sur-

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[1] Extract from thesis for the degree of E.M., Colorado School of Mines, Golden, Colorado. The writer wishes to thank Dr. Herman Fleck, who suggested this method.