allowing vapor molecules to pass freely, but owing to surface tension or some other factors does not allow liquid to pass.

(2) That these membranes are of the nature of gels, and that the outer surface of the gels evaporates and the liquid on the inner surface replenishes, by diffusion, the water thus lost. This theory is in harmony with the fact that ordinary collodion hardens and becomes impermeable when dry, to ordinary dialysis, and also with the fact that all membranes are set or fixed by immersion in water. This fact also indicates that water is a constituent of membranes, either chemically or otherwise, and the rapid drying indicates that this water also has a vapor pressure. Until the solution within a membrane is saturated with a constituent, osmotic pressure seems to prevent any crystallization taking place on the outside. This statement is supported, if not proven, by the fact that percrystallized substances on the outside of the containers will dissolve on adding a little water on the inside. As the crystals are practically dry, and free from mother liquor, percrystallization ought to be useful, not only in many chemical operations heretofore difficult and impossible, but ought to be useful for ordinary crystallization as well. Some crystals, however, seem to have a tendency to puncture the membrane and since different forms of membranes have not been studied, this difficulty perhaps may still be circumvented. It seems probable that other membranes pervaporating other solvents may be found since the usefulness of such a process is now apparent.

IV. Summary.

(1) Collodion and parchment membrane containers permit water to evaporate through the walls as though no membrane were present. This phenomenon is called pervaporation.

(2) Distillation by means of pervaporation is called perstillation, and can be conducted at ordinary atmospheric pressure with low temperatures as well as with vacuum.

(3) When a dialyzable constituent of a liquid within these containers reaches saturation, crystallization usually takes place on the outside. This phenomenon is called percrystallization.

(4) A number of experiments are described which show the possible uses of these phenomena in the arts and sciences. The theoretical considerations of the phenomena are briefly discussed.

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NOTE.

The Reduction of Mercuric Compounds.—In a study of the reduction of mercuric chloride by phosphorous acid and sodium formate, respectively, it was found[1] that concordant velocity constants were obtained

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[1] Linhart, *Am. J. Sci.*, 35, 353 (1913); THIS JOURNAL, 37, 70 (1915).

if the experimental results were substituted in an equation representing a reaction of the second order, although the total reaction as generally written is trimolecular. To account for these facts unstable intermediate compounds were assumed, in the one case H_2PO_3 and in the other —COONa, the reactions being represented by the following equations:

(*a*) (slow reaction), $H_3PO_3 + HgCl_2 = HgCl + H_2PO_3 + HCl$

(*b*) (rapid reaction), $2H_2PO_3 + H_2O = H_3PO_3 + H_3PO_4$.

Similarly:

(*a*) (slow reaction), $HCOONa + HgCl_2 = —COONa + HgCl + HCl$

(*b*) (rapid reaction), $2—COONa + H_2O = HCOONa + NaHCO_3$

(*c*) (rapid reaction); $NaHCO_3 + HCl = NaCl + CO_2 + H_2O$.

In the absence of any data these assumptions, although *ad hoc*, seemed quite as plausible as any other. However, Van Name,[1] very recently having occasion to measure the rate of hydrolysis of hypophosphoric acid in connection with a study of the oxyacids of phosphorus, found that the rate of hydrolysis of hypophosphoric acid was rather slow, so that the assumption with reference to the formation of the unstable H_2PO_3 as an intermediate product in the reduction of mercuric chloride by phosphorous acid becomes untenable.

Since the reducing agents considered are known to be able to reduce mercuric salts to metallic mercury (under the proper conditions) and the reaction of mercuric chloride with metallic mercury to form mercurous chloride is known to be instantaneous even in very dilute solutions, the reactions may be most simply represented by the following equations:

$(a)_1$ (slow), $H_3PO_3 + HgCl_2 + H_2O = H_3PO_4 + 2HCl + Hg$

$(a)_2$ (slow), $HCOONa + HgCl_2 = HCl + NaCl + CO_2 + Hg$

$(a)_3$ (slow), $SnCl_2 + HgCl_2 = SnCl_4 + Hg$

(*b*) (rapid), $HgCl_2 + Hg = Hg_2Cl_2$.

It is, moreover, not *necessary* to assume that metallic mercury is actually formed, as any compound with mercury in the same valence condition and which reacts with $HgCl_2$ will answer,[2] thus:

(*a*) (slow), $HgCl_2 + H_3PO_3 = (HO)_3P(HgCl)Cl$

(*b*) (rapid), $HgCl_2 + (HO)_3P(HgCl)Cl + H_2O = Hg_2Cl_2 + 2HCl + H_3PO_4$.

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[1] Results not yet published.

[2] W. C. Bray has pointed out that these two explanations are not only not incompatible, but may even be regarded as two ways of stating the same thing, for the $HgCl_2$ and the reducing agent can react only when a molecule of one meets a molecule of the other, and during the reaction there will be present a tautomeric addition compound, equivalent on the one hand to $HgCl_2.H_2O.P(OH)_3$ and on the other to $Hg.2ClH.OP(OH)_3$.

On the other hand, it is also not to be supposed that mercury would be *separated* in the metallic condition, as the reaction with $HgCl_2$ is rapid enough so that even the slight solubility of mercury in water is not exceeded.

In general we may represent the reduction of mercuric compounds as going first to mercury, or some substance which behaves like mercury, and then, if conditions permit, to mercurous compounds. This manner of representing the reaction accounts for the fact that it is *bimolecular*, so far as concerns kinetics, and does away with the necessity for specific explanations for each different reducing agent.

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COMMUNICATION ON TAUTOMERISM. ON THE TAUTOMERIC REACTIONS OF 1-PHENYL-4,5-DIHYDRO-5-OXY-3-TRIAZOLYL METHYL SULFONE AND ITS SALTS WITH DIAZOMETHANE AND WITH ALKYL HALIDES.[1]

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Various theories have been proposed to account for the phenomenon of tautomerism, and among them are those of Comstock,[2] Wheeler,[3] Nef,[4] and Michael.[5] One of the facts which these theories try to explain is how two or more stable isomeric products can be obtained by the action of a reagent upon a tautomeric substance. Though these theories have been shown to fit in with the facts excellently in certain cases, yet a large amount of experimental evidence obtained in this laboratory has shown that these theories do not fully correlate the quantitative data obtained with the urazoles.

According to our theory of tautomerism, when urazoles, their salts, and derivatives give two or more stable products as a result of the reaction, they do so because they exist (*a*) in one tautomeric form alone which yields two or more derivatives through independent side reactions,[6] or (*b*) in two or more forms in equilibrium, each of which gives its own derivatives through an independent reaction. The urazole salts or acids could react through their anions or nonionized molecules, or both.

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[1] We have been aided in this work by the Carnegie Institution of Washington.

[2] *Ber.*, **23**, 2274 (1890); *Am. Chem. J.*, **12**, 493 (1890); **13**, 514, 525 (1891).

[3] *Am. Chem. J.*, **21**, 187 (1899); **23**, 135 (1900); **30**, 28 (1903).

[4] *Ann. Chem.*, **258**, 261 (1890); **266**, 105 (1891); **276**, 200 (1893); **277**, 59, 83 (1893).

[5] *J. prakt. Chem.*, **37**, 469 (1888); **45**, 580 (1892); **46**, 189 (1892); *Am. Chem. J.*, **43**, 322 (1910).

[6] For mathematical discussion of this theory, see Acree, *Am. Chem. J.*, **38**, 1 (1907).