

## EVAPORATION OF SOLUTIONS AND LIQUIDS IN BURETTES.

M. G. MELLON, Purdue University.

In very accurate titrametric analyses one may weigh the amount of standard solution reacting with the constituent being determined and from the weight of solution used calculate the percentage of the constituent, providing the concentration of the standard solution has been determined upon a weight basis. This procedure avoids the possible errors arising from a change of temperature and from evaporation, if the standard solution is measured rather than weighed. The volumetric method of determining the amount of solution is, however, the one generally employed.

In the event of a distinct change occurring in the temperature of the standard solution during a determination, which means a corresponding change in the volume of the solution, one needs only to note the variation of temperature and then to consult tables for the proper correction in volume. These tables have been prepared for various solutions of various concentrations.

The error arising from evaporation of the solvent of a standard solution and the consequent increase in concentration of solute per unit volume is not so readily found in the usual works of reference on quantitative chemical analysis. The experiments reported at this time were made with the object of obtaining information regarding the rate of evaporation of solutions and liquids in burettes.

*Factors Affecting the Rate of Evaporation.* No previous work has been found relating directly to the effect upon the accuracy of analytical data resulting from the loss, through evaporation, of the solvent of standard solutions standing in burettes. Many papers have appeared, however, dealing with the general subject of evaporation and with the laws relating to the process,<sup>1</sup> but we are here concerned with a consideration only of the factors affecting the systems now being studied. From these papers just mentioned and from others dealing with certain aspects of the physico-chemical theory of solutions and liquids, a number of facts may be summarized as having a direct bearing upon the present work.

All liquids tend to assume the gaseous phase, and the measure of this tendency is known as the vapor tension of the liquid. For a given liquid there corresponds to each temperature a certain definite pressure of its vapor. This vapor pressure is defined as that pressure at which the rate of escape into the gaseous phase of the liquid molecules is ex-

<sup>1</sup> Livingston—Monthly Weather Report—U.S.A.—1909. "An Annotated Bibliography on Evaporation."

Vaillant—Compt. rend. 146, 582, 811; 148, 1699; 150, 213.

Jablezynski and Prezmyski—J. chim. phys. 10, 241.

Marcelin—*Ibid.*—10, 680.

Marcelin—Compt. rend. 158, 1674.

Thomas and Ferguson—Phil. Mag. 34, 308 (1917).

Burger—Proc. Acad. Sci. Amsterdam—21, 271 (1919).

Weiser and Porter—Jr. Phys. Chem.—24, 333 (1920).

"Proc. 38th Meeting, 1922 (1923)."

actly balanced by the return into the liquid phase of the gaseous molecules. In the event that the system under consideration is not closed and that the rate of escape of the liquid molecules over-balances the rate of return of the gaseous molecules, the equilibrium otherwise prevailing is disturbed and the liquid evaporates.

The rate of the process of evaporation is then subject to several variable factors. In the case of liquid water, for example, exposed in an open vessel to the atmosphere, the rate of evaporation is directly proportional to the velocity of air currents, to the radius of the exposed surface, and to the vapor tension of the liquid. The latter is in turn directly proportional to the temperature. Further, the rate is inversely proportional to the distance of the surface of the liquid from the rim of the containing vessel, to the relative humidity or partial pressure of aqueous vapor of the atmosphere, and to the barometric pressure. Various "laws of evaporation" have been proposed in the effort to connect these variables with the rate of evaporation. Some of the expressions developed include such constants as the molecular weight of the liquid and the latent heat of vaporization, if the rate is to be stated in terms of mass of liquid evaporated per unit time.

In the case of solutions there must be considered also the variation of the vapor pressure of the solvent with the amount of the dissolved solute. It is well known that the vapor pressure of a solvent is lowered by the addition of a soluble salt, for example, and that the retardation in the rate of evaporation thereby produced is proportional to the amount of salt dissolved. Furthermore, it has been shown recently that loss of solvent by evaporation of equimolar solutions is least with salts that give the greatest number of ions.

*Experimental Procedure.* The burettes used in this work were of the type recommended by the Bureau of Standards, and were sealed off at the bottom in order to prevent any error from leakage. Two sets were arranged, the individual members being chosen as nearly as possible with the same inside diameters. Over the "open" set was suspended a cover about 10 cm. from the ends of the burettes in order to protect them from falling particles of dust. Over the ends of the "covered" set were placed ends of test tubes, 6 cm. long, to serve as caps.

The temperature at the time of reading the burettes was taken from a thermometer suspended among them. A sling psychrometer was used for determining the relative humidity of the atmosphere according to the method of the U. S. Weather Bureau. The barometric readings are uncorrected.

Working under the conditions of experimentation stated, determinations have been made of the effect upon the rate of evaporation of (a) the size of the burette, (b) the concentration of solutions, and (c) the presence of caps over the ends of the burettes. For the study of (a) several liquids having distinctly different vapor tensions were selected—water, benzene and toluene; for (b) a series of standard solutions of sodium chloride in water were prepared by dissolving the proper weight of salt; and for (c) parallel series were run for (a) and (b)—one set covered and the other open.

For any given series of readings the burettes were filled and the solutions allowed to attain the temperature of the room. In order to have the surfaces of the solutions in the several burettes all the same distance from the top at the beginning, a siphon extending down 10 cm. from the rim was used to remove any solution or liquid above this point. After a few minutes the first reading was made. The others were taken on the mornings of succeeding days, before the small laboratory was opened and the temperature had an opportunity to change much. The sets were only partially protected from currents of air.

This method of procedure does not furnish data on the actual rate of evaporation for any definite conditions, as no attempt was made to hold any of the variable factors constant during the determinations; but it does furnish one with an approximate idea of the error involved as a result of evaporation of standard solutions under the usual conditions prevailing in the laboratory.

The following tables include the data obtained for solutions of sodium chloride of various concentrations, water, benzene and toluene. The total loss in milliliters is given for the various intervals of time.

TABLE 4. Evaporation of Liquids in Burettes of Different Capacities.

WATER											
Time days	Temp. degrees C.	Relative Humidity	Barometric Pressure mm.	10 ml.		25 ml.		50 ml.		100 ml.	
				Open	Cov- ered	Open	Cov- ered	Open	Cov- ered	Open	Cov- ered
1	21.5	53	752.5	0.01	0.01	0.01	0.00	0.02	0.01	0.02	0.01
2	24.5	31	756.0	0.02	0.01	0.02	0.00	0.01	0.01	0.00	0.02
3	23.0	30	748.7	0.04	0.03	0.05	0.02	0.07	0.02	0.08	0.02
4	23.0	51	746.2	0.07	0.04	0.10	0.05	0.12	0.06	0.20	0.10
5	18.0	57	744.4	0.09	0.05	0.12	0.07	0.11	0.08	0.24	0.12
6	22.0	37	751.1	0.09	0.06	0.13	0.07	0.15	0.08	0.25	0.13
7	23.5	23	754.3	0.11	0.07	0.16	0.07	0.15	0.07	0.20	0.08
8	25.0	26	753.8	0.12	0.08	0.18	0.08	0.16	0.06	0.20	0.06
9	22.5	33	754.5	0.15	0.10	0.22	0.11	0.22	0.12	0.34	0.16
10	19.0	39	754.3	0.18	0.12	0.26	0.13	0.27	0.17	0.46	0.26
12	21.0	39	744.8	0.20	0.14	0.31	0.16	0.32	0.19	0.50	0.30
14	20.0	31	748.7	0.25	0.17	0.37	0.19	0.38	0.23	0.64	0.36
BENZENE											
1	23.5	33	748.5	0.22	0.16	0.37	0.20	0.34	0.23	0.58	0.34
2	23.5	38	755.3	0.44	0.31	0.68	0.39	0.64	0.44	1.14	0.70
3	22.0	33	756.0	0.66	0.49	1.06	0.64	1.07	0.77	1.90	1.30
4	18.0	44	751.4	0.89	0.67	1.44	0.91	1.51	1.13	2.72	1.96
5	18.5	53	752.2	1.06	0.80	1.69	1.06	1.72	1.29	3.08	2.22
TOLUENE											
1	23.5	32	753.0	0.07	0.05	0.10	0.06	0.10	0.07	0.16	0.08
2	24.0	24	746.2	0.13	0.09	0.18	0.10	0.18	0.11	0.30	0.16
3	21.0	22	747.0	0.20	0.14	0.30	0.18	0.30	0.19	0.52	0.30
4	19.0	29	752.0	0.29	0.22	0.49	0.32	0.58	0.44	1.02	0.74
Diameter of Burettes in cm.				0.86	0.86	1.08	1.08	1.06	1.06	1.24	1.24

TABLE 2. Evaporation of Aqueous Solutions of Sodium Chloride of Different Concentrations in Burettes of the Same Capacity.

Time days	Temp. degrees C.	Barometric Pressure mm.	Relative Humidity	Water		0.25 N		0.50 N		0.75 N		1.00 N		2.00 N		5.00 N		
				Open	Cov- ered	Open	Cov- ered	Open	Cov- ered	Open	Cov- ered	Open	Cov- ered	Open	Cov- ered	Open	Cov- ered	Open
1	21.5	752.5	53	0.01	0.00	0.01	0.00	0.01	0.00	0.02	0.01	0.02	0.00	0.01	0.00	0.00	0.00	0.00
2	24.5	756.0	31	0.01	-0.01	0.00	-0.03	0.00	-0.03	-0.01	-0.03	-0.01	-0.04	-0.03	-0.05	-0.07	-0.07	
3	23.0	748.7	30	0.06	0.02	0.04	0.00	0.04	0.02	0.04	0.03	0.05	0.00	0.02	0.00	-0.01	-0.02	
4	23.0	746.2	54	0.11	0.06	0.09	0.04	0.10	0.05	0.10	0.08	0.11	0.04	0.09	0.05	0.05	0.03	
5	18.0	744.4	57	0.14	0.08	0.13	0.07	0.13	0.09	0.14	0.10	0.14	0.07	0.12	0.08	0.09	0.07	
6	22.0	751.1	37	0.14	0.08	0.13	0.07	0.14	0.09	0.14	0.11	0.14	0.07	0.12	0.08	0.09	0.07	
7	23.5	754.3	23	0.14	0.07	0.13	0.05	0.13	0.05	0.13	0.11	0.14	0.07	0.12	0.08	0.09	0.07	
8	25.0	753.8	26	0.14	0.06	0.13	0.04	0.14	0.04	0.13	0.05	0.13	0.00	0.06	-0.01	-0.01	-0.07	
9	22.5	754.5	33	0.21	0.12	0.20	0.10	0.20	0.10	0.19	0.11	0.20	0.08	0.16	0.09	0.10	0.05	
10	19.0	751.3	39	0.27	0.17	0.26	0.14	0.26	0.15	0.26	0.17	0.27	0.14	0.25	0.15	0.18	0.11	
12	21.0	744.8	39	0.31	0.19	0.30	0.15	0.30	0.17	0.30	0.19	0.30	0.15	0.27	0.16	0.19	0.11	
14	20.0	748.7	31	0.38	0.23	0.36	0.19	0.36	0.20	0.36	0.23	0.36	0.18	0.32	0.19	0.22	0.11	
22	24.0	746.0	51	0.54	0.32	0.52	0.25	0.50	0.27	0.50	0.29	0.49	0.23	0.43	0.25	0.29	0.13	
37	22.0	753.2	34	0.89	0.55	0.81	0.46	0.84	0.48	0.85	0.53	0.85	0.44	0.77	0.47	0.57	0.29	
Diameter of Burettes in cm.				1.06	1.07	1.06	1.07	1.03	1.06	1.06	1.06	1.06	1.08	1.06	1.07	1.06	1.06	

*Conclusions.* From the statements already made concerning the several variable factors involved in this work, one would predict certain of the results that are apparent in tables 1 and 2. The rate of evaporation should be greater in the 100 ml. burettes than in those of less capacity having a shorter radius of exposed surface; it should be less for water than for benzene which has, for a given temperature, a higher vapor tension; the vapor pressure of a solution 5N is less than that for one 0.25N, hence the rate should be less for the more concentrated solution; and covers over the ends of the burettes should decrease the rate, due to their partial closing of the systems and consequent prevention of freely circulating air from carrying away the gaseous molecules of the liquids.

On account of the rather complex situation prevailing in these experiments, with the several variable factors uncontrolled, it is not possible to point out the effect of each variation. It seems probable that the effects of changes in barometric pressure and relative humidity are relatively small as compared with that for changes in temperature. An inspection of the results in table 2 for the eighth and ninth days shows a small change of the former variables but a distinct increase in the readings of the burettes, even though a decrease in the temperature should have decreased the vapor tension of the water and thus have decreased the rate of evaporation. It seems evident that a change of temperature of the solutions produces a change of volume considerably larger than the change resulting from a change of vapor tension, and in the opposite direction.

It has already been stated that experiments conducted under the conditions prevailing during this work cannot give entirely satisfactory results, but they do furnish a general basis for predicting what may happen when such measurements are made in the usual laboratory. It is evident that caps on burettes do retard the rate of evaporation; but it is also evident that the total loss through evaporation for an aqueous solution is small at the end of a day, even in the open burettes, and one never takes such a length of time for the ordinary titration. Changes of temperature are liable to cause a much greater change in the volume of a standard solution.

---

## THE USE OF SOLUTIONS OF INORGANIC SALTS AS PERMANENT COLOR STANDARDS.

M. G. MELLON, Purdue University.

In the colorimetric determination of certain substances a common procedure consists in comparing, by means of a colorimeter or some other device suitable for the desired accuracy, a definite volume of a solution containing the unknown substance with various standard solutions containing definite amounts either of the constituent being determined, or of some other substance showing the same color as this constituent. When a match is found between the unknown and one of the standards, it is assumed that the amounts of the color-forming constitu-