

completely metallic circuit, all at one temperature, can give no electromotive force. This is a thermodynamic necessity if there is no process accompanying the passage of a current, except the absorption of heat from the surroundings, which could serve as a source for the electric work. We may, however, construct a new type of concentration cell, composed entirely of metals, which, according to the results of our transference experiments, should give a definite and measurable electromotive force. If we have in contact with one another two sodium amalgams of different concentrations and a platinum electrode in each, we may expect to obtain an electromotive force between the electrodes, owing to the fact that a current passing through such a cell in the right direction will carry the sodium from a region of higher to one of lower concentration. Experiments with such concentration cells are now in progress, and may afford a more exact method of determining the transference number of amalgams.

Summary.

An electric current passing through a dilute amalgam of sodium or potassium causes a transfer of the dissolved metal in the direction of the negative current. The number of equivalents carried per faraday is 2.9×10^{-6} in sodium amalgam of 3.24 atom per cent., and 0.29×10^{-6} in sodium amalgam of 0.577 atom per cent. In potassium amalgam of 2.16 atom per cent. it is 3.6×10^{-6} . An explanation of this transference is offered and the relationship between transference number and electrical conductivity is pointed out.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON.]

MOLECULAR WEIGHTS OF GASES BY AN EVAPORATION METHOD.

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Received September 27, 1915.

Before the researches of Stefan¹ on the rates of evaporation of ether and carbon disulfide into different gases, it was generally believed by physicists that the rate of evaporation of a liquid is independent of the character of the gas above the liquid.² Stefan demonstrated that the velocity of evaporation varies with the nature of the gas above the liquid,

¹ M. J. Stefan, *Wien. Akad. Ber. Math. Naturw.*, 68, 385 (1872). See also *Ibid.*, 63, 163 (1871) and 65, 323 (1872).

² Stefan quotes from Marbach's *physikalischen Lexicon* under the heading, "Verdunstung and Verdampfung," as follows: "Die Natur der Luftarten äussert übrigens keinen Einfluss auf die Verdunstung der Flüssigkeiten, sobald nur die Umstände also der Druck, die Temperatur u. s. w. gleich sind. Mag die Verdunstung in einer Atmosphäre von Sauerstoff, Wasserstoff, Stickstoff, Kohlensäure, oder an der Luft selbst, vor sich gehen, die Menge der entweichenden Dämpfe bleibt sich bei den

and established four laws for the process. His apparatus consisted of capillary tubes of 0.6 to 6.0 mm. bore, and of several centimeters length, filled with ether, and exposed to the air of a room near an open window. No thermostat was employed, and the amount of evaporation was measured by reading the loss in height of the liquid column after a given interval of time.

Stefan did not employ water in his investigation, owing to its slow rate of evaporation and to the variable humidity of atmospheric air, for which it would be difficult to make corrections. He was able to connect the rate of evaporation with the dimensions of the capillary, the temperature, and the vapor pressure of the liquid under consideration. It remained for Winckelmann¹ and Guglielmo² to extend the measurements to include water as well as other liquids. The apparatus of the former consisted of a small test tube fitting snugly into a hole in the bottom of a larger one. The liquid was contained in the smaller test tube and the gas employed was supplied at high velocities by means of a glass tube terminating just at the mouth of the lower test tube. The larger test tube was thus filled with pure gas throughout the course of the experiment. The loss by evaporation was measured by reading the heights of liquid before and after a given time interval.

Winckelmann observed that for many liquids the rates of evaporation depended upon the gas used, being most rapid for hydrogen, and correspondingly slower for the heavier gases. He also calculated diffusion coefficients for the various pairs of substances investigated. The objection to Winckelmann's method is that he used a blast of air, which is not permissible in the measurements of the free diffusion of gases.

Recently P. Vaillant³ has made use of an evaporation method to measure the vapor pressures of solutions. His method is interesting in that it employs a weight-loss rather than a volume-loss method of measuring the amount of evaporation. It is not, however, free from objection, since his loss in weight was invariably less than one milligram.

The object of this investigation was to find a simple and accurate method for the measurement of rates of evaporation of water into different gases, with a view to ascertaining the relation between the rates and the densities of the gases used. The first requirement of the method was that it should eliminate the objections involved in the preceding investigations and provide a perfectly dry atmosphere, immovable, and at a constant

einzelnen Flüssigkeiten, sobald sich die Bedingungen unter denen die Verdunstung stattfindet nicht ändern, gleich. Das ist schon in früherer Zeit durch Volta, Saussure, Dalton, De Luc, und Clement und Desormes nachgewiesen."

¹ Winckelmann, *Ann. Phys. (Wied.)*, 22, 159 (1884).

² Guglielmo, *Beibl.*, 8, 20 (1884).

³ P. Vaillant, *Compt. rend.*, 148, 1099 (1909); see also, W. Müller Erzbach, *Sitzber. K. akad. Wiss. (Vienna) Math. Naturw. Kl.*, 112 (pt. 2a), 615 (1903).

temperature, and that the loss by evaporation should be measured by a weight-loss method and not by a volume-loss method. Water, rather than another liquid, was chosen because of the greater interest attaching to evaporation studies in which water is involved.¹

The apparatus employed in this investigation was very simple. It consisted of a small (3 cc.) flask evaporator, made from 1 to 6 mm. tubing and provided with a glass stopper. This flask contained water, saturated with the gas used. The dry gas was contained in an Erlenmeyer flask in contact with phosphorus pentoxide. At the beginning of an experiment the evaporator was connected with the flask and the whole apparatus was immersed in the thermostat at $25.07^\circ \pm 0.01^\circ$. After several days the apparatus was removed, and the weight of liquid lost from the evaporator, determined. This weight loss divided by the time in hours and multiplied by the barometric height in mm. gives the value for the constant (Col. 5) in the tables. This constant is derived on the basis of the law first formulated by Dalton² that the rate of evaporation is directly proportional to the aqueous tension of the liquid and inversely proportional to the atmospheric pressure. For slight differences in barometric height the law of Dalton gives values for the evaporation constant which agree with each other fully as well as those, calculated on the basis of Stefan's law,³ viz.: $dW/dt = K \log B/B - p$, where B is the barometer reading and p is the vapor tension of the liquid.⁴

Theoretical.—Let us try to picture to ourselves the mechanism by which evaporation takes place from the surface of a pure liquid into an infinite atmosphere of dry gas. At the surface of the liquid, we have a saturated vapor in equilibrium with the liquid. The vapor pressure of the superambient atmosphere is maintained constantly less than at the surface, being of course nil in a perfectly dry atmosphere. Connecting the dry atmosphere with the surface of the liquid is an atmosphere of increasing humidity, completely saturated at all times at the immediate liquid surface.

The rate of evaporation from this surface into a gas is obviously solely dependent upon the relative rates of diffusion of the vapor and of the gas, provided the vapor moves away from the liquid surface, at a rate slow enough not to interfere with the establishment of equilibrium conditions between the vapor and liquid phases. The maintenance of an equilibrium condition at the surface, will in turn depend upon the constancy of tem-

¹ See below. A very complete annotated bibliography on evaporation is furnished by *Monthly Weather Review*, Washington, June, 1908, to June, 1909.

² *Mem. lit. phil. soc.*, 5, 536 (1802).

³ *Loc. cit.*

⁴ The evaporation constants calculated on the basis of Dalton's law deviated from the mean by from 1.4 to 4.5% for a given experiment. Values calculated by means of Stefan's law showed corresponding deviations of from 1.2 to 5%.

perature, the length of the moist atmospheric column, and the absence of violent stirring effects in the gas. If we neglect these precautions we are not at all sure that the surface gas layer is saturated with liquid, and what we measure then, is not in reality the relative rates of diffusion of the two gases, but the combined effects of wind and diffusion.¹ This is equivalent to the statement that evaporation proceeds in two steps, the first a simple change of phase, the second a diffusion of vapor away from the liquid surface.

In this research definite working conditions have been established which yield a measure of the relative diffusion rates by an evaporation method. We should, therefore, anticipate that the velocities will be in harmony with Graham's law of inverse square roots of the densities, and that the method itself, like that of Bunsen, will furnish a means of determination of the molecular weights of gases. The following data represent the results obtained in a series of experiments carried out as above described.

TABLE I.

Gas.	Bottle 1 (6 mm. diam.).			$B \times dW/dT.$
	dW/dT (gms./hr.).	dT (hrs.).	B (corr.).	
Air.....	0.0008836	74.92	750.0	66.31×10^{-2}
Air.....	8623	135.5	754.7	65.06
Air.....	8743	141.42	753.8	65.89
Air.....	856	192.92	756.5	64.76
Air.....	8700	166.25	754.3	65.63
Air.....	8573	144.17	751.0	64.36
	8673			65.34 Mean
CO ₂	0.0006070	144.83	751.2	45.59
CO ₂	6250	147.0
CO ₂	6505	144.83	750.5	48.87
CO ₂	6255	215.1	756.8	47.39
CO ₂	6100	191.1	752.8	45.99
CO ₂	6023	189.3	750.4	45.17
	620			46.60 Mean
H ₂	0.002947	136.2	749.8	221.2
H ₂	296	119.17	752.6	222.7
H ₂	2858	220.8	750.2	214.6
.....	3044	139.6	756.5	230.4
	2952			222.2 Mean

¹ It should be pointed out that as the experiments were conducted the atmosphere held a fixed position throughout, relative to the liquid surface, and that it was water vapor, not air, which steadily diffused.

TABLE I (continued).

Bottle 2 (1 mm. diam.).				
Gas.	dW/dT (gms./hr.).	dT (hrs.).	B (corr.).	$B \times dW/dT$.
Air.....	0.0001142	210.1	750.0	8.59×10^{-2}
Air.....	1128	142.1	753.7	8.50
Air.....	1127	166.8	754.2	8.50
Air.....	1134	144.62	751.0	8.52
	1133			8.52 Mean
H ₂	0.0003991	145.75	751.2	30.00×10^{-2}
H ₂	348	430.47	752.0	26.17
H ₂	361	214.7	756.8	27.32
H ₂	359	190.9	752.8	27.03
H ₂	365	189.3	750.3	27.39
	367			27.58 Mean
CO ₂	0.0000679	137.07	752.6	5.11
CO ₂	816	118.93	752.6	6.14
CO ₂	801	221.0	750.5	6.01
CO ₂	829	475.5	754.6	6.26
.....	707	140.0	756.5	5.35
	766			5.77 Mean
Bottle 3 (4 mm. diam.).				
Air.....	0.000610	145.8	750.2	45.76×10^{-2}
Air.....	608	147.7	750.5	45.63
Air.....	602	430.8	752.0	45.24
Air.....	593	214.3	756.8	44.85
Air.....	594	191.7	752.8	44.73
Mean.....	602			45.24 Mean
CO ₂	0.000445	190.1	756.5	33.67
CO ₂	427	167.3	754.2	32.17
CO ₂	424	145.3	751.0	31.84
Mean.....	432			32.56 Mean
H ₂	0.002220	136.3	752.6	167.0
H ₂	2158	119.0	752.6	162.5
H ₂	2071	220.67	750.5	156.3
H ₂	2052	140.5	759.6	155.2
	2123			160.3 Mean

Calculated on the basis of Graham's law of inverse squares, hydrogen diffuses 3.79 times as fast as air and 4.67 times as fast as carbon dioxide, and air, 1.24 times as fast as carbon dioxide. The results from Table I are as follows:

RELATIVE DIFFUSION RATES.

	H ₂ /Air.	H ₂ /CO ₂ .	Air/CO ₂ .
Bottle 1.....	3.40	4.77	1.40
Bottle 2.....	3.24	4.78	1.48
Bottle 3.....	3.54	4.93	1.39
Mean.....	3.39	4.83	1.42

Further experiments on evaporation are being conducted in this laboratory, and the results of an investigation with a somewhat modified apparatus will be published at an early date.

Applications.—(1) The difference in the rates of evaporation of water into different gases may be used as a method of comparison between the molecular weights of gases. (2) The dependence of rate of evaporation upon the nature of the gas suggests that the feeling of warmth caused by carbon dioxide upon the nerves of the hand¹ may be due to retardation of the normal rate of perspiration. (3) The explanation of higher and more constant terrestrial temperatures in previous geologic eras notably in the carboniferous, may be connected with the slower evaporation of water into an atmosphere rich in carbon dioxide.²

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY.
No. 256.]

THE ELECTRICAL SYNTHESIS OF COLLOIDS.

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Received September 27, 1915.

I. Previous Work.

Since the discovery by Bredig³ of the electrical dispersion method of preparing metallic hydrosols and its modification by Svedberg⁴ for the preparation of metallic organosols, very little conclusive experimental work has been brought forward with the object of a satisfactory explanation of the phenomenon.

Kutscherow,⁵ from a study of the dispersion of bi-metal alloys in alcohol by Svedberg's method, found the amounts of the two metals in the highly dispersed colloidal condition to be proportional to their equivalent weights, and he concluded that the process was of an electrochemical nature, leading to an atomically dispersed condition, which was followed by condensation to the colloidal condition. The thermo-mechanical process

¹ Goldscheider, *Gesammelte Abhandlungen*, 1, 305 (1898).

² See Arrhenius, "Worlds in the Making."

³ *Z. angew. Chem.*, 11, 951 (1898); *Z. Elektrochem.*, 4, 514 (1898).

⁴ *Ber.*, 38, 3616 (1905); 39, 1703 (1906); also "Herstellung Kolloider Lösung Anorganische Stoffe," 1909, p. 423ff.

⁵ *Z. Chem. Ind. Kolloide*, 11, 165 (1912).