change led us to repeat their work and to study the effect of added alkali on many exchanges. Like Winter, Carlton and Briscoe we were completely unable to confirm the effect in the case of sulfate, and are of the opinion that the observations were in error, or were due to exchange with silicate in the glass. We have some slight evidence of catalysis by alkali in the case of chlorate, bromate, iodate and arsenate, but the effects are so slight and the working range in the case of iodate so small (less than 2 γd) that we cannot feel certain that the apparent effects are not due to silicate in the glass, or other experimental error. On the other hand, in the case of nitrate (run 24) perchlorate (run 42) selenate (run 58) and sulfate (runs 68, 69) we found no trace of such an effect of the glass container and a total absence of effect of the added alkali.

Finally, in line with Winter, Carlton and Briscoe's experience, we found that alkali somewhat retarded the exchange of chromate, and we have further found that the presence of 0.2 N sodium hydroxide completely inhibits the otherwise complete exchange of sulfite and thiosulfate.

Summary

1. Extensive density measurements by the method of the magnetically controlled swimmer have been carried out with a routine precision of 0.02 γd and an over-all reproducibility (including the purification of samples) of 0.1 γd.

2. Attention is called to the advantage in comparing the densities of waters or dilute aqueous solutions, of working near the temperature of maximum density of the samples.

3. Oxygen exchange between anions and water enriched in O^{18} was studied at 95–100° in the case of 21 inorganic salts and CrO_3.

4. Resistance to exchange was found to increase toward the upper right-hand corner of the periodic table and with the number of oxygen atoms attached to a given central atom.

5. Many of the exchanges appear to be promoted by excess acid and retarded by excess base.

6. Most of the salts studied exchange completely under the conditions used, several show no exchange at all, and only a few show partial exchange.

Measurement of the Excess Weight of Air Oxygen by Exchange with Inorganic Salts[1]

BY ORVAL R. ALEXANDER AND NORRIS F. HALL

Since its discovery[2] the excess atomic weight of air oxygen (Dole effect) has been measured by numerous authors with fairly consistent results.[3] There has been critical discussion of the various methods used by the different authors but the chief uncertainties seem to be (1) the still imperfectly known degree to which different natural waters differ in density, (2) the possibility that samples even of the "same" water, such as "Lake Michigan," "Atlantic Ocean," or "Lake Mendota" used by different investigators or by the same investigators at different times are significantly different in density, and (3) the possibility of different degrees of isotopic fractionation during the purification of the various samples, particularly as the same purification process produces a slightly different effect on waters of different composition.[4,5,6]

The present paper does not resolve these difficulties, which would require an extensive coöperative program between different laboratories, but merely presents an additional independent method of disclosing and measuring the Dole effect.

The finding that many inorganic salts exchange their oxygen rapidly and completely with water in which they are dissolved, suggested that the Dole effect could be measured by this method. Sodium dichromate appeared to be the most suitable salt.[6]

Procedure.—Reference water was prepared from Lake Mendota water by refluxing with permanganate and alkali for twelve hours, and finally distilled with the rejection of a 3% head and a 2% tail fraction. Samples of this were then purified in the regular way.[6] Several samples of air-oxygen water were prepared as follows. Air was washed

(1) This work was supported in part by grants from the Wisconsin Alumni Research Foundation.

(2) (a) Dole, THIS JOURNAL, **57**, 2731 (1935); (b) *J. Chem. Phys.*, **4**, 268 (1936); (c) Morita and Titani, *Bull. Chem. Soc. Japan*, **11**, 36, 414 (1936).

(3) For literature references see Swartout and Dole, THIS JOURNAL, **61**, 2025–2029 (1939).

(4) Greene and Voskuyl, *ibid.*, **61**, 1342 (1939).

(5) Dole and Slobod, *ibid.*, **62**, 471–479 (1940).

(6) Hall and Alexander. *ibid.*, **62**, 3455 (1940).

with sulfuric acid, dried over soda-lime and magnesium perchlorate, passed through activated charcoal, and filtered through a sintered glass disk. This air was then mixed with an excess of purified tank hydrogen. The hydrogen was passed over a hot copper catalyst to remove any oxygen, then dried over calcium chloride and magnesium perchlorate, and filtered through a tight plug of glass cotton. This mixture of air and hydrogen was passed through a pyrex tube containing a roll of copper gauze. This tube was maintained at 400–500°. Most of the water vapor was condensed in a water-cooled condenser and all but a negligible amount was removed in a freezing train. After purification these two varieties—the air-water and the lake water—were analyzed for heavy oxygen with the aid of interchange between the water and sodium dichromate.

A weighed amount of the thoroughly dried salt was heated with 40 g. of the purified lake water, for four to five hours at 95°. The water was then removed from the salt and the density change determined. The same portion of sodium dichromate was then similarly treated with 40 g. of the air-oxygen water and the change in density determined. It was found that the oxygen of the dichromate was somewhat heavier than that of the lake water, and much lighter than that of the air water.

If h is the density increase of the reference water, d is the density decrease of the air-oxygen water, n is the number of gram atoms of oxygen in each sample of water, and N is the number of gram atoms of oxygen in the salt used, then D, the excess density of air-oxygen water over the reference water is

$$D = \left(\frac{n + N}{N}\right) d + h \; *$$

Since 40 g. of water was always used, n is constant and equal to 2.22. The results of a series of measurements on three different samples of air oxygen are given in Table I. Density changes are in γd.

TABLE I
EXCESS DENSITY OF AIR-OXYGEN WATER (DOLE EFFECT)

Sample	N	d	h	D
1a	2.14	3.15	0.63	7.05
1b	2.14	3.32	.48	7.24
2a	2.18	3.13	.47	6.78
2b	2.27	3.27	.57	7.04
2c	2.28	3.29	.69	7.19
3a	2.21	3.11	.46	6.70
3b	2.27	3.45	.39	7.21
3c	2.34	3.40	.64	7.26

$$7.06 \pm 0.17$$

Density of Various Samples of Water

We made several comparative measurements on four samples of water.

(*) This formula is derived on the simplifying assumption of random distribution of O^{18} between the salt and water at exchange equilibrium.

One was the reference water from Lake Mendota, one was from the Milwaukee city supply (treated Lake Michigan water taken from about a mile off-shore), one was taken from the surface of Lake Michigan at a point on the shore, and one was the artesian well Madison tap water. With the mean density of the reference sample taken as zero all were similarly purified and measured and the results were as shown in Table II.

TABLE II
DENSITY OF WATER FROM VARIOUS SOURCES ($\Delta \gamma d$)

Lake Mendota (reference)	Madison tap	Lake Michigan
+0.24	−0.99	+0.03
− .11	−1.09	+0.21
− .09	−0.65	+0.18
− .25	−0.77	+0.19[a]
− .21		
± .00		
+ .25		
(.00 ± 0.10)	−0.88 ± 0.17	+0.15 ± 0.06

[a] This sample from Milwaukee city supply.

Insofar as comparison is possible, these results do not entirely agree with any of the others. Thus while we find Lake Mendota water 0.15 γd lighter than that of Lake Michigan, Hall and Jones[7] found it 0.3 γd lighter and Greene and Voskuyl[4] found it 0.16 γd *denser*. The Madison City water (from artesian wells) which Hall and Jones found 0.25 γd lighter, we find 0.88 γd lighter. If we accept the conclusion of Greene and Voskuyl[4] that tap water everywhere in the temperate zone is substantially identical, our results on the two lakes are not very different from theirs. Thus the density of Lake Mendota on this scale would be +0.88, +0.77, average +0.83 γd, while that of Lake Michigan would be +1.03, +0.66, average +0.85. On the assumption that two-thirds of this difference is due to oxygen, a correction of two-thirds of 0.88 or 0.59 γd should be added to our result, making the final value 7.65 ± 0.2 γd. A final correction must await further results.

Summary

1. A method is described for determining the density difference due to oxygen alone of two samples of water. This consists in causing them successively and completely to exchange oxygen with a dissolved oxygen compound which contains no hydrogen.

2. Exchange experiments were carried out with air-oxygen water and Lake Mendota

(7) Hall and Jones, THIS JOURNAL, **58**, 1915 (1936).

water in exchange with sodium dichromate.

3. The excess density due to air oxygen is 7.65 ± 0.2 γd if Madison city water is regarded as nor-

mal in isotopic composition, or 7.1 ± 0.2 γd if Lake Mendota water is normal.

MADISON, WISCONSIN   RECEIVED JULY 12, 1940

Thermal Data. XIII. The Heat Capacities and Entropies of Creatine Hydrate, dl-Citrulline, dl-Ornithine, l-Proline and Taurine

BY HUGH M. HUFFMAN AND SIDNEY W. FOX

In continuation of our program[1] involving the study of thermal properties of organic compounds of physiological interest, we have determined the heat capacities of creatine hydrate, dl-citrulline, dl-ornithine, l-proline and taurine in the temperature range 90 to 298°K. These data have been used in conjunction with the extrapolation formula of Parks, Kelley and Huffman[2] to calculate the entropies of these compounds at 25°.

Experimental

In principal the method of Nernst was employed with an aneroid calorimeter to determine the "true" specific heat. The details of the method have been described elsewhere[3] so that only a brief account need be given. In brief it consists in supplying, electrically, a measured amount of energy to a gold calorimeter containing the substance under investigation. To ensure rapid attainment of thermal equilibrium, the substance is pressed into dense pellets, about 2 mm. thick, and spaced along the centrally located thermocouple well by means of thin gold disks which are in good thermal contact with the walls of the calorimeter. The electrical measurements of current and voltage are made on a "White" double potentiometer by the proper use of accurately calibrated resistances. Time measurements are made by means of a calibrated stop watch. The temperature measurements are made by means of the White potentiometer in conjunction with a single junction copper–constantan thermocouple. This couple is periodically standardized against one of the couples calibrated in the investigation of Giauque, Johnston and Kelley.[4]

Materials.—Creatine hydrate from Eastman Kodak Company was once crystallized from water. Nitrogen determinations by macro-Kjeldahl indicated a purity of 99 to 100%.

dl-Citrulline was prepared by the alkaline hydrolysis of arginine.[5] The material thus obtained was crystallized from a hot aqueous solution by the addition of several volumes of ethyl alcohol. Determination of amino nitrogen by formol titration gave 99% of the theoretical.

dl-Ornithine was synthesized from arginine flavianate as

the starting material by a method the details of which will be published in a separate communication. Determination of C, H and N indicated a purity between 96 and 100%. This material is extremely hygroscopic, thus causing considerable uncertainty in the analytical data.

TABLE I

HEAT CAPACITY PER GRAM OF SUBSTANCE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
		Creatine Hydrate			
87.3	0.1326	155.5	0.2051	258.8	0.3052
92.0	.1380	172.8	.2222	273.6	.3189
97.2	.1435	190.1	.2402	279.9	.3259
103.1	.1507	210.0	.2600	285.6	.3306
109.7	.1576	226.3	.2749	297.2	.3366
116.5	.1649	242.9	.2909	298.4	.3423
136.3	.1852				
		dl-Citrulline			
89.4	0.1261	157.3	0.1889	264.8	0.2844
95.7	.1324	177.3	.2069	277.5	.2957
101.7	.1383	181.5	.2222	283.9	.3022
110.1	.1463	207.9	.2335	290.5	.3076
125.5	.1608	223.5	.2483	300.8	.3176
140.7	.1740	239.4	.2622		
		dl-Ornithine			
88.6	0.1237	178.6	0.2131	277.1	0.3096
94.6	.1298	193.7	.2276	283.3	:3175
100.0	.1364	209.1	.2423	288.5	.3274
109.5	.1464	223.8	.2563	290.8	.3324
126.0	.1633	237.0	.2681	298.0	.3441
144.1	.1821	263.8	.2951	298.1	.3460
156.3	.1933	277.0	.3087		
		l-Proline			
87.7	0.1223	154.2	0.1811	247.0	0.2630
94.8	.1286	171.8	.1969	257.5	.2724
101.3	.1348	189.1	.2119	276.8	.2892
108.3	.1411	204.0	.2257	283.2	.2947
116.5	.1478	219.2	.2390	291.8	.3027
125.1	.1555	237.3	.2549	300.4	.3096
		Taurine			
87.3	0.1039	159.7	0.1663	249.9	0.2326
92.8	.1089	178.1	.1806	263.7	.2425
97.9	.1138	183.4	.1926	276.3	.2508
112.6	.1274	208.0	.2037	281.8	.2547
123.9	.1373	221.9	.2136	293.0	.2630
140.7	.1516	236.4	.2236	300.3	.2684

(1) Huffman and Borsook, THIS JOURNAL, 54, 4297 (1932).
(2) Parks, Kelley and Huffman, J. Phys. Chem., 33, 1802 (1929).
(3) Parks, THIS JOURNAL, 47, 338 (1925).
(4) Giauque, Johnston and Kelley, ibid., 49, 2367 (1927).
(5) Fox, J. Biol. Chem., 123, 687 (1938).