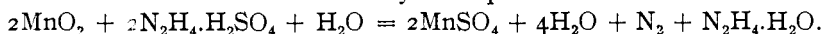


Purgotti<sup>1</sup> has recommended the general use of hydrazine sulphate for the gasometric determination of oxidizing agents, relying upon the assumption that the oxidation of hydrazine takes place with quantitative evolution of nitrogen. The action of manganese dioxide upon hydrazine sulphate in acid solution is expressed by this investigator with the aid of the equation:

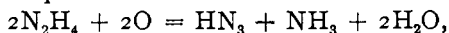
$$2\text{MnO}_2 + \text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4 = 2\text{MnSO}_4 + 4\text{H}_2\text{O} + \text{N}_2 + \text{H}_2\text{SO}_4,$$

and the action in neutral solution by the equation:



### Summary.

The maximum yields of hydronitric acid and ammonia obtained under specified conditions by the action of certain oxidizing agents upon hydrazine sulphate in aqueous solution, and calculated (when given as percentages) from the equation



are as follows:

(1) With potassium persulphate in acid solution, 40.3 per cent.  $\text{HN}_3$ , 1.5 molecules  $\text{NH}_3$  from 2 molecules of  $\text{N}_2\text{H}_4$ ; in alkaline solution, small amounts of  $\text{HN}_3$ , and about 20 per cent. of  $\text{NH}_3$ .

(2) With potassium permanganate in acid solution, 3.19 per cent.  $\text{HN}_3$ , 1.65 molecules  $\text{NH}_3$  from 2 molecules  $\text{N}_2\text{H}_4$ ; in alkaline solution, small amounts of  $\text{HN}_3$ .

(3) With hydrogen peroxide in acid solution, 38.5 per cent.  $\text{HN}_3$ , 1.10 molecules  $\text{NH}_3$  from 2 molecules of  $\text{N}_2\text{H}_4$ ; in alkaline solution, small amounts of  $\text{HN}_3$ , fairly large amounts of  $\text{NH}_3$ .

(4) With potassium perchlorate in acid solution, 22.4 per cent.  $\text{HN}_3$ , 44.0 per cent.  $\text{NH}_3$ .

(5) With sodium periodate in acid solution, considerable quantities of hydronitric acid and ammonia, when silver sulphate was present.

(6) With lead dioxide in acid solution, 4.1 per cent.  $\text{HN}_3$ , 13.2 per cent.  $\text{NH}_3$ .

(7) With red lead,  $\text{HN}_3$  and  $\text{NH}_3$  in acid solution.

(8) With manganese dioxide in acid solution, 2.32 per cent.  $\text{HN}_3$ , 1.53 molecules  $\text{NH}_3$  from 2 molecules  $\text{N}_2\text{H}_4$ .

CORNELL UNIVERSITY, November, 1908.

## THE WEIGHT OF CARBON DIOXIDE WITH A TABLE OF CALCULATED RESULTS.

By S. W. PARR.

Received December 3, 1908.

In making use of analytical methods involving the evolution and measurement of constituents in the gaseous form, two difficulties are met

with: first, the apparatus ordinarily available may not have the desired degree of accuracy, and second, the tables and factors for reducing the gas volume to gravimetric terms may be in error. It is the purpose of this note to deal with the second phase of the matter only and to consider the values for carbon dioxide.

In 1863, Dietrich<sup>1</sup> described a method for liberating and measuring carbon dioxide, but gave only a method for calculating the weight by formula, using a unit value of 1.9774 grams per liter at 0° and 760 mm. pressure and assuming an arbitrary barometric pressure for all conditions, namely, 760 mm. In the year following, he revised this method and introduced a table which took account of variations in the barometric pressure.<sup>2</sup> There is no intimation in this second article, or in any subsequent note, as to what initial value was used for the gas. It would be assumed, therefore, that the same value was employed as was indicated in his work of the year previous, 1.9774. But this will not satisfy the conditions of the table. No explanation is given in the context for using a different value, and indeed no hint is given that a change has been made, but by calculation, the value employed is found to be 1.9678. In this calculation, a correction is introduced for the pressure of water vapor but not for the barometer, since this is all that is indicated by the formula used in the article of the year previous.

It is worth while to call attention to the above facts, for the reason that this table is the one ordinarily met with in reference texts. It was first made use of by Fresenius in his "Quantitative Analysis," edition of 1869, and is the one repeated in manuals of reference such as Biedermann's "Kalender," "Laboratory Calculations" by Adriance, etc., etc.

Recently, a volume of "Physico-Chemical Tables"<sup>3</sup> has appeared, having newly calculated values for carbon dioxide. On pages 354 to 357, inclusive, are tables giving the weight of carbon dioxide in one liter of the moist gas as measured, the calculations being made for temperatures ranging from 0° to 30° and for pressures from 710 mm. to 770 mm. This is the most elaborate table to be found for this gas and it is unfortunate that the values are so wide of the truth. Nor is the error of minor size, being over six units in the second decimal place and representing about three and one-half per cent. of variation from the correct value. The carrying out of the factors, therefore, to the sixth decimal is wasted energy. The sources of error in this table are not readily evident. The factor seemingly decided upon as being the initial value for dry carbon dioxide at 0° and 760 mm. is 1.965161. This factor seems to be used without

<sup>1</sup> *Z. anal. Chem.*, 3, 162.

<sup>2</sup> *Ibid.*, 4, 142.

<sup>3</sup> "Physico-Chemical Tables." Vol. 1, "Chemical Engineering and Physical Chemistry," by Castell-Evans, Griffin & Co., 1903.

correction for water vapor as the starting point for building up the table. But the caption for the table indicates that it is intended to give the weights "for CO<sub>2</sub> saturated with Aqueous Vapor." At that point, however, in the table where values appear for the gas at 0° and 760 mm., the value indicated is 1.965161, which is the value for dry gas as given by Landolt and Börnstein at unit temperature and pressure.

To still further confuse matters, there is given in another part (p. 317), the usual Dietrich table for carbon dioxide as above described. While no explanation in the heading intimates the state in which the gas is to be read or the unit factor on which it is based, the values are presumably those for the moist condition as we have seen above from the reference to his original articles. The two tables, therefore, should agree. Comparing a given reading, however, as for example, at 10° and 760 mm. we find in the newly calculated table (p. 355) a value of 1.814163 and in the old table (p. 317) for the same temperature and pressure, the value given is 1.87430. Numerous attempts to reconcile these two tables have been fruitless.

The question now arises as to the accuracy of the values given in the Dietrich table. With an initial value for the dry gas at 0° and 760 mm. of 1.9678 grams per liter, it is of interest at this point to compare the values as given by more recent authorities.

COMPARISON OF VALUES AS GIVEN FOR 1 LITER OF DRY CARBON DIOXIDE AT 0° AND 760 MM. PRESSURE.

Landolt and Börnstein <sup>1</sup> .....	1.9652
Hempel for latitude 45 <sup>2</sup> .....	1.9650
Hempel for Berlin <sup>3</sup> .....	1.9663
Treadwell <sup>4</sup> .....	1.9650
Wells for latitude 41 <sup>5</sup> .....	1.9641
Compare Dietrich as above given.....	1.9678

It will be seen from this table that a fair agreement exists between the value employed by Dietrich and those of present-day authorities.

But as will be shown further on, Dietrich's figures are in error by about 0.4 of 1 per cent. and the average of the other values is in error by a little over 0.6 per cent. This arises from the method of deriving the initial values. Treadwell, for example (p. 303), says: "In order to compute the weight of carbon dioxide, it is only necessary to remember that a gram molecule of any substance in the gaseous form at 0° and 760 mm. pressure occupies a volume of 22.391 cc." The weight of a gram molecule of carbon dioxide divided by this constant will give the unit weight thus:

<sup>1</sup> Landolt and Börnstein, 3rd Edition, 1905, p. 223.

<sup>2</sup> Hempel's "Gas Analysis," 3rd Edition, Trans. by Dennis, p. 482.

<sup>3</sup> Hempel's "Gas Analysis," 3rd Edition, Trans. by Dennis, p. 201.

<sup>4</sup> "Analytical Chemistry," Treadwell, Trans. by Hall, Vol. II, p. 308.

<sup>5</sup> "Chemical Calculations," Wells, p. 9.

$$\frac{44}{22.391} = 1.9650.$$

But the assumption is wrong and the statement incorrect, for carbon dioxide does not so exactly obey Boyle's law. The observed rather than the theoretical data is the only correct basis for calculating the weight of this gas, hence, the true value should be found by taking the relative density of carbon dioxide, air being unity, and multiplying the unit weight for air by that factor. Thus, if we take for air the value as given by Rayleigh,<sup>1</sup> of 1.29284 and the relative density for carbon dioxide by the same authority, as 1.52909, we shall have  $1.29284 \times 1.52909 = 1.9769$ , as the value for carbon dioxide. A further confirmation of the correctness of this value is afforded by Guye<sup>2</sup> who has recently determined directly the weight of carbon dioxide and gives as the mean of his values, the number 1.9768. Since this is between the values indicated by Rayleigh (1.9769) and that of Leduc (1.9763) he seems to be justified in adopting it as his final value. Correcting this value for the latitude of  $41^\circ$  and an elevation of 100 meters,<sup>3</sup> we shall have the accepted value for 1 liter of pure dry carbon dioxide at  $0^\circ$  and 760 mm. pressure of 1.9760 grams.

It remains to decide upon the coefficient of expansion that shall be applied in calculating values for the gas at observed temperature and pressure.

If Guye, for example, made use of a different coefficient from the one usually applied of 0.00367, then the same coefficient should be used in calculating back to working temperatures. By correspondence with Professor Guye<sup>4</sup> it appears that his determinations were made at  $0^\circ$ . This leaves the question of a coefficient still open.

Chappuis<sup>5</sup> in his study of expansion coefficients gives for carbon dioxide at constant volume and temperatures from  $0-40^\circ$ , a coefficient for 518 mm. of 0.0036972 and for 998 mm. of 0.0037299. By interpolating midway or at a pressure of 758 mm. the observed ratio of expansion per degree of temperature would be 0.0037135. This coefficient, therefore, would seem to be the proper one to introduce into the formula instead of the one applicable to other gases of 0.00367. From all of the con-

<sup>1</sup> *Proc. Royal Soc.*, **62**, 204 (1897).

<sup>2</sup> *J. chim. phys.*, April, 1907. *THIS JOURNAL*, **30**, 155.

<sup>3</sup> The latitude of  $41^\circ$  is less than  $\frac{1}{2}^\circ$  from New Haven, New York, Pittsburgh, Urbana, Ill., Lincoln, Neb., Salt Lake City, etc. See Wells's "Chemical Calculations," p. 47.

<sup>4</sup> " \* \* \* toutes les mesures de densités du gaz  $\text{CO}_2$  résumées, p. 223 de mon article, ont été effectuées à la température de  $0^\circ \text{C}$ .; aussi bien celles de Lord Rayleigh, de M. Leduc que celles que j' ai faites avec M. Pintza. Il n' a donc pas été nécessaire de faire intervenir dans les réductions aucune valeur du coefficient de température."

<sup>5</sup> *Trav. et Mém. du Bur. intern. des Poids et Mes.*, XIII, 190 (1903).

WEIGHT OF CARBON DIOXIDE.

In milligrams per cubic centimeter. Calculated from 1.976 = weight of 1 l. CO<sub>2</sub> at 0° temperature, 760 mm. pressure and 41° latitude. Corrected for aqueous vapor and barometer readings on glass scale.

t/mm.	720.	722.	724.	726.	728.	730.	732.	734.	736.	738.	740.	742.	744.
10	1.7788	1.7838	1.7888	1.7938	1.7988	1.8038	1.8089	1.8139	1.8189	1.8239	1.8288	1.8338	1.8388
11	1.7706	1.7756	1.7806	1.7856	1.7905	1.7955	1.8005	1.8055	1.8105	1.8155	1.8204	1.8254	1.8304
12	1.7623	1.7673	1.7723	1.7773	1.7822	1.7872	1.7921	1.7971	1.8021	1.8071	1.8120	1.8170	1.8219
13	1.7540	1.7590	1.7639	1.7689	1.7738	1.7788	1.7837	1.7887	1.7936	1.7986	1.8035	1.8085	1.8134
14	1.7457	1.7506	1.7555	1.7605	1.7654	1.7703	1.7752	1.7802	1.7851	1.7901	1.7950	1.7999	1.8048
15	1.7373	1.7422	1.7471	1.7520	1.7569	1.7618	1.7667	1.7717	1.7766	1.7815	1.7864	1.7913	1.7962
16	1.7288	1.7337	1.7386	1.7435	1.7484	1.7533	1.7582	1.7631	1.7680	1.7729	1.7778	1.7827	1.7875
17	1.7203	1.7252	1.7301	1.7349	1.7398	1.7447	1.7496	1.7545	1.7593	1.7642	1.7691	1.7740	1.7788
18	1.7117	1.7166	1.7215	1.7263	1.7312	1.7360	1.7409	1.7458	1.7506	1.7555	1.7603	1.7652	1.7700
19	1.7031	1.7079	1.7128	1.7176	1.7225	1.7273	1.7321	1.7370	1.7418	1.7467	1.7515	1.7564	1.7612
20	1.6944	1.6992	1.7041	1.7089	1.7137	1.7185	1.7233	1.7282	1.7330	1.7378	1.7426	1.7475	1.7523
21	1.6856	1.6904	1.6953	1.7001	1.7049	1.7097	1.7145	1.7193	1.7241	1.7289	1.7337	1.7385	1.7433
22	1.6767	1.6815	1.6863	1.6911	1.6959	1.7007	1.7055	1.7103	1.7151	1.7199	1.7247	1.7295	1.7342
23	1.6678	1.6726	1.6773	1.6821	1.6869	1.6917	1.6964	1.7012	1.7060	1.7107	1.7155	1.7203	1.7250
24	1.6587	1.6635	1.6682	1.6730	1.6778	1.6825	1.6872	1.6920	1.6968	1.7015	1.7063	1.7111	1.7158
25	1.6495	1.6543	1.6590	1.6638	1.6685	1.6732	1.6779	1.6827	1.6875	1.6922	1.6969	1.7017	1.7064
26	1.6403	1.6450	1.6497	1.6544	1.6591	1.6638	1.6685	1.6733	1.6780	1.6827	1.6874	1.6922	1.6969
27	1.6309	1.6356	1.6403	1.6450	1.6497	1.6544	1.6591	1.6638	1.6685	1.6732	1.6778	1.6826	1.6873
28	1.6213	1.6260	1.6307	1.6354	1.6401	1.6448	1.6494	1.6541	1.6588	1.6635	1.6681	1.6729	1.6776
29	1.6116	1.6163	1.6210	1.6256	1.6303	1.6350	1.6396	1.6443	1.6490	1.6537	1.6583	1.6630	1.6677
30	1.6018	1.6065	1.6111	1.6157	1.6204	1.6251	1.6297	1.6343	1.6390	1.6437	1.6483	1.6530	1.6577

## WEIGHT OF CARBON DIOXIDE.

In milligrams per cubic centimeter. Calculated from 1.976 = weight of 1 l. CO<sub>2</sub> at 0° temperature, 760 mm. pressure and 41° latitude. Corrected for aqueous vapor and barometer readings on glass scale.

t/mm.	746.	748.	750.	752.	754.	756.	758.	760.	762.	764.	766.	768.	770.
10	1.8439	1.8489	1.8539	1.8589	1.8639	1.8689	1.8739	1.8789	1.8839	1.8890	1.8940	1.8990	1.9040
11	1.8354	1.8404	1.8454	1.8504	1.8554	1.8603	1.8653	1.8703	1.8753	1.8803	1.8853	1.8903	1.8953
12	1.8269	1.8319	1.8368	1.8418	1.8468	1.8517	1.8567	1.8617	1.8667	1.8716	1.8766	1.8816	1.8865
13	1.8184	1.8233	1.8282	1.8332	1.8382	1.8431	1.8481	1.8530	1.8580	1.8629	1.8679	1.8728	1.8777
14	1.8098	1.8147	1.8196	1.8246	1.8295	1.8344	1.8394	1.8443	1.8492	1.8541	1.8591	1.8640	1.8689
15	1.8011	1.8060	1.8109	1.8159	1.8208	1.8257	1.8306	1.8355	1.8404	1.8453	1.8503	1.8552	1.8601
16	1.7924	1.7973	1.8022	1.8072	1.8120	1.8169	1.8218	1.8267	1.8316	1.8365	1.8414	1.8463	1.8512
17	1.7837	1.7886	1.7934	1.7984	1.8032	1.8081	1.8130	1.8178	1.8227	1.8276	1.8325	1.8374	1.8422
18	1.7749	1.7798	1.7846	1.7895	1.7944	1.7992	1.8041	1.8089	1.8138	1.8187	1.8235	1.8284	1.8332
19	1.7661	1.7709	1.7757	1.7806	1.7854	1.7902	1.7951	1.7999	1.8048	1.8096	1.8144	1.8193	1.8241
20	1.7571	1.7619	1.7667	1.7716	1.7764	1.7812	1.7861	1.7909	1.7957	1.8005	1.8053	1.8102	1.8150
21	1.7481	1.7529	1.7577	1.7625	1.7673	1.7721	1.7770	1.7818	1.7866	1.7914	1.7962	1.8010	1.8058
22	1.7390	1.7438	1.7486	1.7534	1.7582	1.7630	1.7678	1.7725	1.7773	1.7821	1.7869	1.7917	1.7965
23	1.7298	1.7346	1.7394	1.7441	1.7489	1.7537	1.7585	1.7632	1.7680	1.7728	1.7776	1.7823	1.7871
24	1.7206	1.7253	1.7301	1.7348	1.7396	1.7443	1.7491	1.7538	1.7586	1.7633	1.7681	1.7728	1.7776
25	1.7112	1.7159	1.7206	1.7254	1.7301	1.7348	1.7396	1.7443	1.7490	1.7538	1.7585	1.7633	1.7680
26	1.7016	1.7063	1.7110	1.7158	1.7205	1.7252	1.7300	1.7347	1.7394	1.7441	1.7488	1.7535	1.7582
27	1.6920	1.6967	1.7014	1.7061	1.7108	1.7155	1.7202	1.7249	1.7296	1.7343	1.7390	1.7437	1.7484
28	1.6822	1.6869	1.6916	1.6963	1.7010	1.7057	1.7104	1.7150	1.7197	1.7244	1.7291	1.7338	1.7385
29	1.6723	1.6770	1.6817	1.6864	1.6910	1.6957	1.7004	1.7050	1.7097	1.7144	1.7191	1.7237	1.7284
30	1.6623	1.6670	1.6716	1.6763	1.6809	1.6856	1.6903	1.6949	1.6996	1.7042	1.7089	1.7135	1.7182

siderations above enumerated it would seem worth while to calculate a new table making use of the values as indicated.

A summary of the factors entering into the calculation is as follows:

*Observed* weight of 1 liter  $\text{CO}_2$  at  $0^\circ$  and 760 mm. Guye—Lat.  $45^\circ$  (*J. chim. phys.*, April, 1907), 1.9768.

*Corrected* value for  $\text{CO}_2$ ; Lat.  $41^\circ$ , elevation 100 meters.  $1.9768 \times 0.9996007$ ; 1.9760.

Coefficient of expansion for  $\text{CO}_2$ . Constant volume—Chappuis 1903, 0.0037135.

Formula used:

$$V = \frac{v (P - w - b)}{760 (1 + 0.0037135 \times t)},$$

in which  $P$  is the observed pressure; ( $w$ ) is the correction for tension of aqueous vapor; ( $b$ ) correction for barometer, glass scale.

Hence the formula for  $W$  (weight) of 1 liter observed volume reduced to  $0^\circ$  and 760 mm. would be

$$W = \frac{1.976 (P - w - b)}{760 (1 + 0.0037135 \times t)}.$$

The accompanying table has been calculated on this basis.

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## THE NON-EXISTENCE OF TELLURIUM OXYCHLORIDE.

BY VICTOR LENHER.

Received November 18, 1908.

According to Ditte<sup>1</sup> when  $\text{TeO}_2\text{HCl}$  is heated above  $300^\circ$ , decomposition ensues with the formation of tellurium oxychloride and water, thus:  $\text{TeO}_2\text{HCl} = \text{TeOCl}_2 + \text{H}_2\text{O}$ .

This statement has been carried through the literature without modification and the oxychloride is described as light brown leaflets which melt to a dark liquid and which dissociate easily giving volatile tellurium chloride and a residue of dioxide.

That such a compound as  $\text{TeOCl}_2$  should exist might be deduced from its analogues  $\text{SOCl}_2$  and  $\text{SeOCl}_2$ . The latter, oxychloride of selenium, is readily prepared by heating molecular proportions of selenium dioxide with the tetrachloride. When tellurium dioxide is heated with tellurium tetrachloride no definite compound is produced. Indeed carefully conducted experiments have shown us that when equal parts of tetrachloride and dioxide are heated in carbon dioxide, the dioxide remains non-volatile and is practically chlorine-free while the chloride volatilizes. When tellurium tetrachloride is heated alone in the air it gradually loses chlorine and is finally converted into the dioxide, which is chlorine-free.

<sup>1</sup> *Compt. rend.*, 83, 336.