present writer tried carbon tetrachloride, benzene and nitrobenzene. A solution of iodine monochloride in dilute hydrochloric acid was diluted with water and rapidly shaken with the inert solvent before hydrolysis had gone far. No iodine monochloride could be found in the solvent, and no difference in the oxidizing power of the aqueous layer on potassium iodide could be detected before and after extraction.

While the present results do not allow a final decision on the many factors which may influence equilibrium in this system, the most probable view is that the positive iodine is in the form of a complex anion ICl_2^-, and that at great dilution this ion suffers partial dissociation into I^+ and Cl^-. In concentrated hydrochloric acid the concentration of iodine cation must be negligible, and some other explanation must be sought for the solvent power of these solutions on iodine noted in a previous paper. As to the titration of iodine in concentrated hydrochloric acid with an iodate, calculation from the observed values of K_1 shows that a very small excess of iodate is sufficient to reduce the equilibrium concentration of iodine below the level at which it can be detected—*i. e.*, the end-point is very sharp. This is in agreement with experience. The high acid concentration used in the titration is not necessary to reduce hydrolysis but is needed to make the reaction a rapid one, as already noted by Swift.[4]

Summary

1. The equilibrium between iodine monochloride and water at 25° has been investigated quantitatively.

2. The results indicate that in chloride solutions iodine monochloride is present chiefly as a complex ion ICl_2^-, which at great dilutions suffers dissociation into I^+ and Cl^-. In concentrated hydrochloric acid this dissociation is negligible.

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[4] Swift, THIS JOURNAL, 52, 894 (1930).

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[CONTRIBUTION FROM THE THERMOCHEMICAL LABORATORY, INORGANIC DEPARTMENT, UNIVERSITY OF LIVERPOOL]

Systematic Investigation of a Hitherto Undetected Source of Error in Chemical Measurements of High Precision which Depend upon the Use of Compressed Oxygen. I

BY L. J. P. KEFFLER

Introduction.—The accuracy of the results obtained with the calorimetric bomb for the heats of combustion of organic substances depends in a large measure upon the accuracy with which the water equivalent of the calorimetric system has been determined. The water equivalent, in turn, or at least its apparent value, depends upon the amount of combustible impurity contained in the oxygen used for the combustion. Hitherto it has been assumed that no error was introduced into the measurements as the result of such contamination of the oxygen, on the condition that the amount of impurity be slight and that the same oxygen be used for the determination of a heat of combustion as had been used previously for the determination of the water equivalent.[1]

It is now going to be shown that such a procedure is not safe, since the oxygen delivered from a newly refilled cylinder may vary quite appreciably in purity when the pressure in the cylinder decreases.

(1) **Data Obtained with Oxygen (G) from Unknown Origin.**—A first series of measurements of the water equivalent of the calorimeter was carried out with standard benzoic acid from the Bureau of Standards, using oxygen from a hundred-foot cylinder supplied by the British Oxygen Company; the source of the gas could not be ascertained. The results obtained with that oxygen (G) have been collected in Table I.

(2) **Data Obtained with Oxygen (K) Derived from Liquid Air.**—A request was made to the British Oxygen Company to deliver two hundred-foot cylinders of the purest oxygen from liquid air which they could possibly supply. Both of these cylinders (K and L) when tested with a view to finding whether they were really identical, gave the same value for the water equivalent when this was determined under similar conditions. This appears clearly from Table II which contains besides the results corresponding to the new cylinders, those obtained previously with oxygen E (preheated) and oxygen G (unheated).

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[1] Richards, THIS JOURNAL, 42, 1604 (1920).

Table I

Values Obtained for the Water Equivalent with Oxygen G for a Pressure of 35 Atm. in the Bomb and Various Pressures in the Cylinder

Press. in cyl. (atm.)	123:121	85:72	58:52	34:26
Water equiv.	4278.4	4274.7	4274.7	4271.6 and 4274.1
	4277.7	4275.5	4276.3	4274.0 and 4273.1
	4277.3	4275.5	4275.2	4273.0 and 4273.9
	....	4274.1	4276.3	4272.0 and 4275.8
	....	4275.0	....	.....
Mean (exptl.)	4277.8	4275.0	4275.5	4273.4
Mean (standardized)	4277.1	4275.7	4274.8	4274.1

Table II

Values Obtained with Various Cylinders (L, K, G and E) for the Water Equivalent, Expressed in Cal.$_{15}$/Degree, for a Pressure of 35 Atm. in the Bomb

Oxygen	L	K	K	G	E
Benzoic acid burnt	No. 48a	48a	39b	39b	39c
Press. in cylinder	121:102	116:113	112:109	123:121	(preheated)
Water equiv.	4277.6	4276.3	4276.8	4277.7	4277.4
	−6.9	−6.5	−7.0	−7.0	−8.0
	....	−7.8	−6.5	−6.6	−6.3
	....	−7.4	−8.7	....	−5.6
	....	....	....	....	−8.0
Mean	4277.2	4277.0	4277.2	4277.1	4277.1

It is hardly to be hoped that the agreement between all these means could be improved upon and there is thus conferred an exceptionally high character of trustworthiness on the value 4277.1 obtained for the water equivalent as the mean of means from eighteen combustions carried out in five independent series of calibration experiments. Furthermore, since oxygen E has been purified by preheating, the value obtained by its means should represent the true value for the water equivalent; and the circumstance that the other values were found equal to that relative to oxygen E carries with it the conclusion that these other oxygen samples were apparently quite as pure as the purified oxygen E, although they had not been subjected to a preheating treatment. Indeed, by using oxygen freed from combustible impurities, the thermal effect will be a minimum and consequently the corresponding water equivalent will be a maximum; but, by making use of oxygen which is contaminated with some combustible impurity, the apparent water equivalent will be lower than the true one, and the more so, the greater the amount of impurity.

The remarkable agreement secured with the cylinders L, K, G and E did not however last over the whole life of these cylinders: indeed, when the calibration was repeated with oxygen K, first over the same range of 2.6° and then over a range of only 2°, the oxygen being delivered while the pressure in the cylinder gradually decreased to the pressure of 35 atmospheres required for the filling of the bomb, different results were obtained; these have been collected in Table III.

From the higher value (4277.1) obtained for the water equivalent at the higher pressures, to the lower value (4275.2) found at the lower pressures in the cylinder, there is a gradual drop of 2 calories, which is equivalent to 5 parts in 10,000 and is thus only slightly less than the similar lowering found previously in the case of oxygen G (7 parts in 10,000). Apart from this difference of about 2 parts in 10,000, relative to the change in water equivalent observed from the higher to the lower pressures, the behavior of the two samples K and G of oxygen is closely comparable, as will appear from Table IV.

It would thus seem very probable that oxygen G (of unknown origin), being characterized by exactly the same initial value (4277.1) for the water equivalent as oxygen K (from liquid air) and by a final value (G:4274.1) only just smaller than the corresponding one (4275.2) for oxygen K, and exhibiting all through its life a very similar behavior to that of oxygen K, was like the latter derived from liquid air.

(3) The Nature of the Combustible Impurities Present in Commercial Oxygen.—According

TABLE III

VALUES OBTAINED FOR THE WATER EQUIVALENT WITH OXYGEN K, FOR VARIOUS PRESSURES IN THE CYLINDER AND A PRESSURE OF 35 ATMOSPHERES IN THE BOMB

Range, °C.	2.6	2.6	2.0	2.6	2.0	2.0
Press. in cyl.	116:109	93:87	92:88	59:55	66:64	54:39
Water equiv. (exptl. values)	4277.2	4277.6	4276.9	4277.1	4275.8	4275.8
	7.4					
	8.7	6.5	6.1	7.0	6.1	6.1
	8.3					
	7.7	7.9	6.9	7.4	4.9	6.0
	7.9					
	7.4	8.2	7.5	6.6	6.4	
	9.6					
Mean water equiv. (isothermal)	4277.1	4276.6	4276.2	4276.1	4275.1	4275.3
					4275.2	
Mean error for mean (in parts per mille)	0.06	0.09	0.06	0.04	0.08	0.02

TABLE IV

MEAN VALUES OBTAINED FOR THE WATER EQUIVALENT WITH OXYGEN G OR K

Press. in cylinder	115	90	90	75	55	45	30
Mean water equiv. (for oxygen G)	4277.1	....	....	4275.7	4274.8	....	4274.1
No. of combustions	3	....	....	4	5	....	8
Mean water equiv. (for oxygen K)	4277.1	4276.6	4276.2	....	4276.1	4275.3	....
No. of combustions	8	4	4	....	4	3	....

to Gauthier[2] air normally contains about 1 to 2 parts by volume of hydrogen per 10,000 parts of air, together with small quantities of methane, varying between the wide limits of 22.6 (in Paris) to 0 parts per 100,000 (above the ocean). In the most unfavorable case where the whole of that maximum amount of methane would find its way into the oxygen compressed into the cylinder, the maximum error possibly entailed for each combustion of calibration, assuming each time the combustion in the bomb to be complete, may be calculated as follows. A bomb of 450-cc. capacity, when filled to 35 atmospheres, will contain approximately 16 liters of oxygen and consequently 22.6 parts per 100,000 would correspond to a maximum amount of 3.6 cc. of methane. Since the molar heat of combustion of methane is 210,800 cal., the combustion of 3.6 cc. of methane (at N. T. P.) would evolve 210,800 × 3.6/22,400 = 34 calories; hence a water equivalent of about 4000 cal. would be characterized by an error of 34 in 4000, *i. e.*, about 8 per mille. Since methane boils at −161.4°, which is only about 20° higher than the boiling point of oxygen (−183°), it is quite possible that an appreciable proportion of methane will distil simultaneously with the oxygen. Even if it were assumed that only about an eighth of the maximum possible amount of 3.6 cc. of methane would contaminate the 16 liters of oxygen in the bomb the error would still be of the order of 1 per mille, which is much larger than the experimental error with a quite up-to-date technique.

Besides these data which were obtained from the literature, the following information was obligingly supplied by the British Oxygen Company: "the firm can supply on special application oxygen extracted from the air by liquefaction, and having a purity not less than 99.5% (the remaining 0.5% being approximately made up of argon 99% and nitrogen 1%); this should not contain any combustible impurity or only the slightest trace, difficult to detect and originating from the lubricating oil used in the air compressors; as for the hydrogen normally present in the air, this passes off with the nitrogen fraction."

The problem for solution now sums up to this: assuming tentatively that cylinders G and K (either believed to be or known to be derived from liquid air) were contaminated mainly with methane (or higher hydrocarbons), how can the fact be accounted for that the gaseous mixture changed quite measurably as regards its content of

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(2) Gmelin-Kraut, "Handbuch der anorganischen Chemie," 1907, Vol. 1, p. 58.

combustible impurity all through the life of the oxygen cylinder?

(4) **Interpretation.**—The explanation which appeared most promising was that the differences in density of the oxygen and of the admixed impurities might in some way be responsible for the phenomenon. It is reasonable to suppose that each of the components of the oxygen mixture in the cylinder effuses through the small aperture in the valve of the bomb more or less in accordance with Graham's law. Each component of the mixture should then have a velocity directly proportional to the square root of the difference between its partial pressures in the cylinder and in the bomb, and inversely proportional to the square root of its density. It should however be observed at once that the conditions prevailing in the filling of the bomb prior to a combustion will never be such as are required for the accurate application of Graham's law, since the aperture in the valve of the bomb is much larger than the orifice (about 0.01 mm. in diameter) which is pierced in the platinum diaphragm of the apparatus used to verify the law with precision. Consequently the results obtained with the bomb should lie somewhere between those which one would expect if the compressed oxygen behaved in all respects as a homogeneous mixture, and those which would be obtained if Graham's law were strictly obeyed.

It should be observed also that the filling of the bomb with oxygen does not as a rule proceed until equilibrium is reached between the partial pressures of the oxygen in the cylinder and in the bomb. In the case of the impurity, however, the conditions are quite different since the impurity will flow into a space originally void but into which it gradually diffuses until either equilibrium is reached between the corresponding partial pressures of this impurity in the cylinder and in the bomb, or until the filling of the bomb is stopped. If the impurity happens to possess a partial pressure and a density such that its rate of effusion is too slow to allow of an equilibrium of pressure being established between the cylinder and the bomb before the filling of the latter is completed, the concentration of the impurity with respect to that of the residual oxygen in the cylinder will gradually increase with each filling of the bomb and consequently the apparent value for the water equivalent will decrease for the subsequent combustions.

This is just what has been found in the case of both oxygen G and K, so that it may be accepted, at least provisionally, that Graham's law applies qualitatively to the phenomenon recorded. It will be the object of a later paper to examine whether the phenomenon will always repeat itself in exactly the same way with any other sample of commercial oxygen.

Summary

1. It has been shown that in the calorimetric bomb the concentration of a combustible impurity eventually present in the oxygen may vary appreciably with the pressure of the gas in the cylinder.

2. It has been suggested tentatively that the variation in the apparent value for the water equivalent with the pressure in the cylinder was possibly governed, at least from a qualitative point of view, by Graham's law of effusion.

Conclusions.—In bomb calorimetry of high precision it is essential to guard against serious errors arising from the slight contamination of the oxygen by combustible impurities, by adopting one of the following precautions: (1) either purify the oxygen by a suitable preheating, prior to its introduction into the bomb; (2) or carry out the calibration and the actual combustions of the substance investigated directly after one another, or, better still, alternate the two series of measurements; (3) or, if the number of combustions with a particular substance were going to be large, repeat the calibration at suitable intervals of the effective life of the cylinder of oxygen in use, say at the beginning, toward the middle and just before the end.

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