polation formulas give results for $\frac{dp_s}{dT}$ at the critical point which are considerably too low. In fact, he finds that at the critical point $\frac{dp_s}{dT} = \frac{2R}{v_c}$. This result is in perfect agreement with the Dieterici equation, for if we substitute the value $\frac{2R}{v_c}$ for $\frac{dp_s}{dT}$ in our formula $a = v_1v_2T\frac{dp_s}{dT}$ we obtain for the critical point, $a_c = 2v_cRT_c$, a relation easily deducible from the Dieterici equation.

TABLE I.—ISOPENTANE UNIT MASS = 1G.

$t°$.	dps/dT.	$a_1 \times 10^{-6}$.	$a_2 \times 10^{-6}$.	$a_3 \times 10^{-6}$.	$a_4 \times 10^{-6}$.	$a_5 \times 10^{-6}$.
0	11.17	4.713	4.704	4.708	2.223	4.292
20	21.02	4.583	4.582	4.582	4.450	4.217
40	35.65	4.461	4.466	4.467	4.434	4.175
60	55.67	4.354	4.353	4.354	4.310	4.115
80	81.90	4.248	4.236	4.242	3.987	4.071
100	114.5	4.150	4.120	4.135	3.747	4.006
110	133.9	4.093	4.059	4.075	3.727	3.970
120	155.4	4.036	3.991	4.012	3.650	3.954
130	178.7	3.977	3.922	3.948	3.604	3.894
140	204.2	3.916	3.860	3.881	3.564	3.832
150	232.9	3.850	3.771	3.806	3.512	3.801
160	263.8	3.778	3.690	3.726	3.480	3.725
170	298.4	3.687	3.599	3.633	3.459	3.624
180	335.7	3.579	3.503	3.528	3.436	3.459
187.8 (Critical temperature)	367.7	3.404	3.423	3.423	3.423	3.087

Summary.

In the present paper, it is shown that the Dieterici equation of state is of the correct form and that it degenerates into the equation of van der Waals for a gas under low pressure. The equation of Dieterici might therefore be expected to have a much wider range of validity than one of the van der Waals type.

A new method of calculating a is described and the values so obtained are compared with those calculated by other methods.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

DIFFERENTIAL IODIMETRY IV.—THE ANALYSIS OF PYROLUSITE AND OTHER OXIDIZED MANGANESE ORES.

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In a previous paper[1] a method has been described for the determination of the available oxygen in precipitated higher oxides of manganese

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and it has also been applied to the analysis of certain ores. This method is excellent whenever it can be applied. However, certain ores are not easily decomposed within a reasonable period of time by treatment with phosphoric acid and potassium iodide. In this paper is given a method of more general application to oxidized ores.

When potassium iodide is added with hydrochloric acid to pyrolusite a very rapid reaction occurs liberating iodine and converting the manganese to manganous chloride. The reaction is completed in a comparatively short time. Ferric iron in hydrochloric acid solution also reacts with potassium iodide liberating iodine, and this reaction is utilized for the quantitative determination of iron or iodine. For the purposes of this work it may be assumed that ferric iron is present in more or less amounts in all manganese ores and therefore would produce a commensurate error in any method involving the direct titration of the iodine thus liberated in a hydrochloric acid solution.

In neutral solution the reaction is reversed, becoming differential toward ferrous iron and manganous manganese, the former being completely oxidized to the ferric state by a slight excess of iodine, while the manganese remains bivalent. When equivalent amounts of iodine and ferrous iron react in neutral solution, some time is required for the reaction to go to completion. In the presence of an excess of iodine the oxidation of the ferrous iron is for all practical purposes an instantaneous one. This condition is always produced when manganese dioxide reacts with iodide in acid solution and the solution is subsequently made neutral.

If one attempts to prepare a neutral solution of ferrous and ferric iron, hydrolysis occurs, precipitating the iron to a greater or less extent. This is prevented by the presence of tartrates. When a neutral tartrate is added to a solution containing a mineral acid, tartaric acid is formed, and in the presence of potassium salts the insoluble potassium acid tartrate may form. In consequence of this, sodium salts are preferable to potassium salts.

The completeness of the oxidation of ferrous iron in neutral solution by iodine was first studied. A known volume of standard iodine, together with 2 g. of powdered sodium tartrate, was added to a measured volume of ferrous sulfate solution (see Table I), and allowed to stand for about five minutes. An excess of sodium bicarbonate was then added, the solution diluted to 150 cc., and the free iodine titrated with standard arsenite solution. The results show that within the errors of the titration all of the ferrous iron was oxidized to the ferric state by iodine in the neutral tartrate solution.

Utilizing the above principle, a method has been devised for the analysis of available oxygen in pyrolusite. The ore should be pulverized to pass 200 mesh and dried at 110° for one hour preceding analysis. A 0.2

g. sample is treated in a 300-cc. Erlenmeyer flask with 10 cc. of 1 *N* sodium iodide (or potassium iodide) solution followed by 5 cc. of concentrated hydrochloric acid. The flask, covered with a watch glass, is allowed to stand with frequent shaking until the reaction has gone to completion. 0.2 to 0.5 g. of pulverized sodium tartrate is added and the solution diluted to about 150 cc. Sodium bicarbonate is added in small amounts until the acid is neutralized, followed by a considerable excess of this reagent. The mechanical loss of iodine due to the evolution of carbon dioxide is negligible provided the sodium bicarbonate is not introduced into the flask too rapidly. The free iodine is now titrated with standard arsenite solution, using starch as the indicator.

TABLE I.—OXIDATION OF FERROUS IRON BY IODINE IN NEUTRAL SOLUTION.

1 cc. of Ferrous Sulfate Solution = 0.004902 g. Fe.

Exp. no.	Cc. $FeSO_4$.	Grams iron. Present.	Grams iron. Found.
1..........	0.00	0.0000	0.0000
2..........	0.00	0.0000	0.0000
3..........	1.00	0.0049	0.0054
4..........	1.00	0.0049	0.0053
5..........	2.00	0.0098	0.0100
6..........	2.00	0.0098	0.0100
7..........	5.00	0.0245	0.0249
8..........	5.00	0.0245	0.0248
9..........	10.00	0.0490	0.0495
10..........	10.00	0.0490	0.0494

TABLE II.—ANALYSIS OF NATURAL OXIDES OF MANGANESE FOR AVAILABLE OXYGEN.

Exp. no.	Percent available oxygen found. Ferrous sulfate method.	Percent available oxygen found. Iodimetric method.
1...........	13.53	13.38
2...........	12.96	12.92
3...........	12.61	12.48
4...........	12.22	12.12
5...........	12.82	12.80
6...........	16.07	16.07
7...........	11.95	11.83
8...........	12.79	12.66
9...........	10.34	10.22
10...........	15.62	15.63

In Table II are tabulated typical results obtained by the method as above outlined and also the results obtained on these ores by the ferrous sulfate method.

With low-grade ores in which the percentage of iron is high, considerable care must be exercised in order to obtain complete decomposition. In such cases, after the titration has been completed, one can always observe a small amount of unattacked ore. Should one desire, the solution may be carefully decanted and the treatment of the residue repeated. In the evaluation of low-grade pyrolusite ores the allowable error in an analysis is such that any discrepancy in the method from this source would ordinarily not be a serious one. The same source of error occurs in the other methods of analysis of such ores. With high-grade products the method gives excellent results.

Summary.

1. Ferrous iron is oxidized completely to the ferric state by an excess of iodine in a neutral tartrate solution. Manganous manganese is not affected under these conditions.

2. This principle is utilized in a direct iodimetric determination of the available oxygen in pyrolusite.

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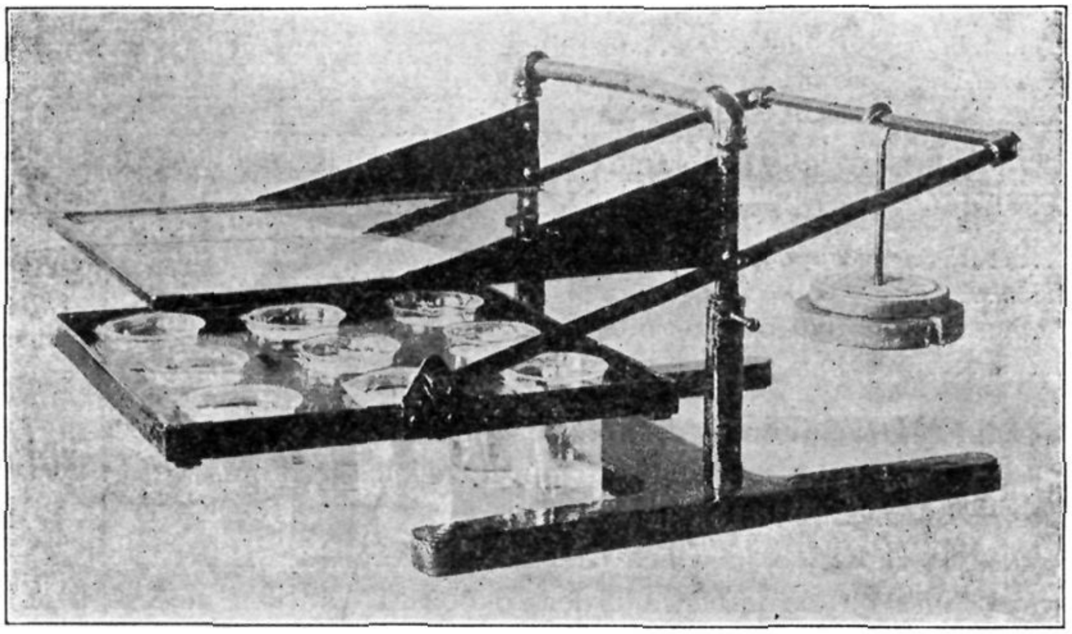
NOTES.

A Simple Device for Evaporating Solutions to a Definite Volume.— In analytical laboratories it is frequently necessary to evaporate a number of solutions simultaneously to a given volume. Ordinarily, such evaporations require more or less attention in order that the beakers may be removed from the source of heat at the proper time and before the evaporation has gone too far.

The simple device here described enables the analyst to perform as many as nine evaporations at one time, starting with the same volume in each beaker and evaporating approximately to any desired volume. When the desired volume is reached, the beakers are automatically removed from the source of heat (steam box or electric hot plate) and covered with a glass plate. The evaporations may therefore be made overnight without risk of any of the beakers going dry, and thus a considerable saving of time is effected.



The principle upon which it operates is that of a balance. The beakers which contain the liquid are placed in one arm of the balance. When sufficient water has evaporated the containers are lifted from the source of heat by the weights attached to the opposite arm of the balance. In order to have all of the beakers contain the same amount of solution at the end they must start with equal amounts.

Referring to the cut, B is an "H" shaped cast iron base, $^1/_2$ inch thick.