the carburization of molybdenum by methane at 700 and 850° and have shown that an abrupt phase change occurs at about 5.9% carbon, *i. e.*, when molybdenum carbide (Mo_2C) is completely formed. Whereas at 700° subjection to further carburization leads to a metastable carbide of higher carbon content, at 850° equilibrium involving direct decomposition to free carbon (to which the carbide of higher carbon content is metastable) sets in. These results are compatible with those of the present contribution.

The value of the equilibrium constant for their reaction

$$2Mo + CH_4 = Mo_2C + 2H_2 \tag{4}$$

may be calculated from those of Reactions 1 and 3, and that of the reaction

$$CH_4 + CO_2 = 2CO + 2H_2$$

The value for the latter, $K_{1083} = 216.2$, was derived by interpolation of the combination of Kassel's[19] values of $R \ln K$ for the formation of methane and of Gordon's[20] values of $R \ln K$ for the decomposition of carbon monoxide into graphite and carbon dioxide. These lead to K_{1083} for Reaction 4 equal to 3454, and $N_{CH_4} = 0.0003$. The results of Schenck, Kurzen and Wesselkock indicate values of approximately 0.004 and 0.001 at 700 and 850°, respectively. In view of the different character of the latter's experiments and the number of steps combined the agreement is satisfactory.

Summary

1. At 400° the reduction of molybdenum trioxide by carbon monoxide is very slow. The end-product of the reduction is apparently molybdenum dioxide, but no runs were made to establish this conclusion definitely.

2. At 560° molybdenum is reduced by carbon monoxide to molybdenum carbide and the carbide catalyzes the decomposition of carbon monoxide.

3. At 810° molybdenum dioxide is reduced to molybdenum carbide (Mo_2C). The over-all reaction is reversible and may be represented by the equation

$$2MoO_2 + 6CO = Mo_2C + 5CO_2$$

The equilibrium constant, K_p, at 810°, calculated on the assumption that the measurements were at 750 mm. pressure, is 1.46.

UNIVERSITY, VIRGINIA RECEIVED AUGUST 1, 1934

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(19) L. S. Kassel, THIS JOURNAL, **55**, 1357 (1933).

(20) A. R. Gordon, *J. Chem. Phys.*, **1**, 308 (1933).

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 145]

Equilibrium in the System Vanadium Tetroxide–Carbon Monoxide–Vanadium Trioxide–Carbon Dioxide

BY HUGH M. SPENCER AND JOHN L. JUSTICE[1]

There has recently been published a study[2] of equilibria in which the reactions are assumed to be

$$^1/_2V_2O_2 + H_2 = V + H_2O \tag{1}$$

$$V_2O_3 + H_2 = V_2O_2 + H_2O \tag{2}$$

which may prove to be a satisfactory means of defining the free energies of formation of vanadium compounds. The dissociation pressure of vanadium pentoxide[3] has also been studied, and values have been reported[4] for the reactions

$$V_2O_4 + H_2 = V_2O_3 + H_2O \tag{3}$$

$$V_2O_5 + H_2 = V_2O_4 + H_2O \tag{4}$$

This latter work appears to be unsatisfactory and the present investigation, in which the reversible equilibrium

$$V_2O_4 + CO = V_2O_3 + CO_2 \tag{5}$$

was studied over the temperature range 750 to 896° by a flow method, was undertaken as part of a program of determining the free energy relations of the vanadium oxides. These are of interest in vanadium oxide catalysis involving oxidation, as well as that involving reduction where the method of production of the catalyst indicates the presence of the lower oxides.[5]

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(1) Du Pont Research Fellow, 1932–1934.

(2) M. Kobayashi, *Bull. Chem. Soc. Japan*, **8**, 231 (1933).

(3) E. F. Milan, *J. Phys. Chem.*, **33**, 498 (1929).

(4) H. Müller, W. Biltz's Festschrift, Hannover, 1927, quoted in J. W. Mellor's "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, Vol. IX, 1929, pp. 741 and 744.

(5) J. M. Weiss, C. R. Downs and R. M. Burns, *Ind. Eng. Chem.*, **15**, 965 (1923); (a) O. W. Brown and C. O. Henke, *J. Phys. Chem.*, **26**, 272 (1922); and H. A. Doyal and O. W. Brown, *ibid.*, **36**, 1549 (1932). Incidentally it may be noted that the first-named authors used an incorrect form of the Nernst approximation equation (in which the heat effect was not doubled in expressing log p_{O_2}) in the calculation of the dissociation pressures of vanadium pentoxide and vanadium tetroxide.

Experimental Method

The apparatus, preparation of the gases and general experimental procedure were the same as those described in the preceding article,[6] except that the temperatures were measured with a thermocouple throughout and except as hereinafter noted.

Materials and Preliminary Experiments.—In the analysis of the vanadium oxides the samples were brought into solution by heating with a small quantity of 10% sulfuric acid. Both the pentoxide and tetroxide will dissolve in acid of this concentration on heating, but to bring about the solution of the trioxide it is necessary to add an oxidizing agent. Dilute potassium permanganate solution was used since the presence of manganous ions in the solution did not interfere with the succeeding steps in the analysis. The solution was diluted until the sulfuric acid content was about 2%. From this point the analysis followed the procedure given by Hillebrand and Lundell.[7]

Technical vanadium pentoxide was the source of the vanadium trioxide used in the preliminary experiments. It was first treated with a few cc. of concentrated nitric acid and heated to expel the excess acid. The oxide was digested with ammonium carbonate solution, and to the filtrate was added saturated ammonium chloride solution, precipitating ammonium metavanadate. The precipitate, after being washed with ammonium chloride solution and dried at 100°, was decomposed by heating in a stream of oxygen for one hour at 400°. The product was an orange powder which analyzed 56.26% vanadium. A 14-g. sample was reduced by passing pure carbon monoxide over it as indicated.

Time in hours from first analysis	0	3
Rate of flow, cc. per min.	19.3	18.8
Temp., °C.	513	494
% CO_2 in exit gas	84.3	52.8

At the time of the first analysis carbon dioxide had been passed over the sample for approximately two hours, roughly one hour required to reach 513°, and one hour at that temperature. On the next day, with approximately the same rate of flow and after equal periods at 498°, the percentages of carbon dioxide were 2.46 and 0.51. The stream of carbon monoxide was continued in each case while the furnace was cooling. The product of the reduction analyzed 66.87% vanadium. The percentage of vanadium in the pure trioxide is 67.98.

Preliminary experiments were next performed with this oxide with the object of determining a suitable temperature range for the study of Reaction 5. At 495° a flow of 26 cc. of carbon dioxide per minute caused the evolution of only 0.13 g. of carbon monoxide in twenty-one minutes, corresponding to 0.2%, and at 705° with a flow of 17.6 cc. of carbon dioxide per minute the exit gas was 0.37% carbon monoxide.

Rough calculations based on Müller's data lead one to expect more than 50% carbon monoxide at the latter of these temperatures. The actual amount found was so small that it seemed desirable to demonstrate its presence, even, by another method of analysis. The reduction, by the exit gas, of palladium chloride, as described by Brody and Millner[8] proved the presence of carbon monoxide.

To make sure that free carbon was not responsible for the presence of carbon monoxide in the exit gas a new sample of vanadium trioxide was prepared by heating C. P. ammonium metavanadate in air and reducing in a current of hydrogen for fourteen hours. Tank hydrogen, purified by passage over copper immersed in ammonium chloride–ammonium hydroxide solution, then through cleaning solution and over soda lime and calcium chloride, was used. Previous to the reduction the silica tube used to hold the oxide was thoroughly cleaned and heated to a bright red heat for four hours in a slow stream of air. During the last half hour of this heating period calcium chloride tubes attached to the reaction tube showed no increase in weight.

This newly prepared oxide, which was also used in the final measurements, was heated in a stream of carbon dioxide. The tests with palladium chloride paper were similar to those made on the trioxide prepared by reduction with carbon monoxide. Below 480° there was no blackening within half an hour, but above that temperature there was blackening. The higher the temperature the less was the time required to bring about the effect.

Vanadium tetroxide was prepared by heating vanadium trioxide in a porcelain dish over a Bunsen burner. When the bottom of the dish became a dull red, a red glow spread throughout the oxide mass and continued for about a minute after the burner was removed. The tetroxide prepared in this way was a dark blue powder and the vanadium content of the different samples prepared varied considerably. One sample prepared by heating a mass of the trioxide about 1.25 cm. thick contained 60.7% vanadium, while a sample prepared by heating a mass 2.5 cm. thick analyzed 62.2% vanadium. The percentage of vanadium in vanadium tetroxide is 61.43. A sample of the tetroxide free from the other oxides of vanadium cannot be prepared by this method for the tetroxide on continued heating in air forms pure vanadium pentoxide, if the heating is conducted below the melting point of the pentoxide. Above the melting point a mixture of the pentoxide and tetroxide results. The samples used were prepared from the trioxide used in the final measurements and are appropriately designated there.

Final Measurements.—Due to the small concentrations of carbon monoxide involved in the study of Reaction 5 the conduct of the equilibrium measurements differed in two respects from that described in the preceding paper: the method of analysis for carbon monoxide and the manner of mixing the gases.

The carbon monoxide was determined by the method of Vandaveer and Gregg.[9] The 0.001 normal sodium thiosulfate used was standardized each day against a fresh 1 to 100 dilution of 0.02 vol.-molal potassium permanganate solution. The 0.5% starch solution was prepared fresh each day. The number of cc. of sodium thiosulfate

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[6] H. M. Spencer and J. L. Justice, THIS JOURNAL, **56**, 2301 (1934).

[7] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, 1929, p. 359.

[8] E. Brody and T. Millner, *Z. anorg. allgem. Chem.*, **164**, 86 (1927).

[9] F. E. Vandaveer and R. C. Gregg, *Ind. Eng. Chem., Anal. Ed.*, **1**, 129 (1929).

used in the titration of the liberated iodine ranged from fifteen to forty five.

More satisfactory mixing of the gases than that effected by the T-stopcock of the previous investigation was found necessary. The stopcock was replaced by a 100-cc. bulb which the gases entered at right angles. With this arrangement satisfactory checks were obtained in blank runs on the inlet and exit amounts of carbon monoxide.

Seventeen grams of the vanadium trioxide previously described was heated in an atmosphere of carbon dioxide at 800° for several days in order that measurements might be made on a partially oxidized surface. The measurements of Table I followed in the order given with the exceptions noted. Analyses made during any one period of heating are grouped together.

TABLE I

MEASUREMENTS IN WHICH THE INITIAL SOLID PHASE WAS VANADIUM TRIOXIDE

Temp., °C.	Rate of flow, cc. per min.	Inlet volumes, cc. CO_2	cc. CO	Outlet volume, cc. CO	p_{CO_2}/p_{CO}
a. Measurements at 820°					
815	19.10	477.4	0	2.175	218
815	18.62	465.5	0	2.177	213
820	19.00	570.0	0	2.598	218
819	19.67	590.1	0	2.811	209
820	19.46	583.8	0	2.843	204
820	19.29	578.7	0	2.837	203
822	7.44	223.2	0	1.072	208
820	8.71	261.3	0	1.251	208
820	7.96	238.8	0	1.110	214
819	35.02	525.3	0	2.039	257
823	35.20	528.0	0	2.335	225
823	34.70	520.5	0	2.328	223
821	14.26	427.8	0	2.034	209
823	14.47	434.1	0	2.046	211
822	14.70	441.0	0	2.082	211
823	14.22	426.6	0	1.886	225
820	13.54	406.2	0	1.818	222
819	13.54	406.2	0	1.813	223
815 ± 2.2	20.08	497.5	4.5	2.393	209
818	20.35	503.8	5.5	2.399	211
825[a]	14.75	442.5	0	1.888	233
824[a]	13.61	408.3	0	1.752	232
821[a]	15.50	465.0	0	1.940	239
822[a]	16.11	483.3	0	2.116	227
821[a]	15.81	474.3	0	2.017	234
				Average for 820°	220
b. Measurements at 896°					
896	13.65	409.5	0	3.164	128
896	13.59	339.8	0	2.495	135
895	14.81	296.2	0	2.186	134
896	13.39	267.8	0	1.913	139
896	13.95	279.0	0	1.944	143
897	14.30	286.0	0	1.978	144
896	14.08	281.0	0	1.866	150
898	12.03	290.8	10.0	2.052	146
899	13.35	298.8	10.0	2.141	143
894	12.27	296.3	10.5	2.114	144
897	12.26	237.2	8.0	1.843	132
896	13.41	272.0	9.7	9.63	[b]
898	13.44	268.8	0	3.747	70.7[c]
892	13.19	263.8	0	2.796	93.3[c]
895	13.56	271.2	0	2.617	103.0[c]
896 ± 5	14.31	286.2	0	2.419	117[c]
896	13.93	278.6	0	2.113	131
894	13.64	272.8	0	1.892	143
894	13.02	260.4	0	1.785	145
896	13.32	266.4	0	1.960	135
896	14.45	291.0	0	2.033	142
897	13.49	269.8	0	1.925	139
891	16.59	331.8	0	2.302	143
Average for 896° (excluding the values denoted by [c])					140
c. Measurements at 750°					
753	16.04	529.3	0	1.411	374
752	13.79	413.7	0	1.106	373
749	18.97	569.1	0	1.441	394
749	17.99	539.7	0	1.422	379
750	18.01	540.3	0	1.423	379
				Average for 750°	380
d. Measurements at 780°					
779	17.43	522.9	0	1.739	300
779	16.79	503.7	0	1.699	295
782	15.00	450.0	0	1.515	296
780	15.72	477.6	0	1.593	295
				Average for 780°	297
e. Measurements at 850°					
848	15.00	375.0	0	1.792	208
850	16.90	507.0	0	2.736	184
851	15.25	457.5	0	2.500	182
851	15.80	489.8	0	2.558	190
851	15.93	477.9	0	2.549	187
851	14.59	437.7	0	2.362	184
851	9.44	283.2	0	1.513	186
848	9.55	286.5	0	1.540	185
848	9.49	256.2	0	1.307	195
				Average for 850°	189

[a] These measurements near 820° were made after those at 850°.

[b] It is not surprising that so few measurements from the carbon monoxide side completely reduced the oxide to the trioxide. The method of making these runs was to heat the sample in a stream of carbon dioxide to the desired temperature and then to run in carbon monoxide at a rate of flow approximately equal to that of the carbon dioxide. After allowing some ten or fifteen minutes for an appreciable concentration of carbon monoxide to be built up throughout the system, the flow of carbon monoxide was reduced to about 0.4 cc. per minute, and the gas mixture passed through the tube for at least three hours before the first analysis was made.

[c] See comments under Discussion.

Following the last measurements at 820° an attempt was made to measure the equilibrium by starting with a sample rich in vanadium tetroxide and building up the trioxide by reduction. The tetroxide was prepared from the sample as described above and subjected to carbon monoxide at 750° for two hours to remove any pentoxide that might have been present. The flowmeters were then reset and after the mixture indicated in the table had been passing for two hours the first analysis of Table II was obtained. An attempt, followed qualitatively by the color of the iodine in the potassium iodide solution, to eliminate the "surface effect," overshot the mark, as complete reduction was indicated.

The sample was reoxidized in air to 62.2% vanadium, thus an appreciable amount of vanadium trioxide (13% if only the trioxide and tetroxide were present) was present, as was also made evident by the fact that the sample was not completely soluble in hot 10% sulfuric acid. The remainder of the experiments of Table II except the last three were made with this sample. The column labeled "Time" is an estimate of the time during which the gas was passing over the sample at a temperature near 750° previous to the analysis. Since the furnace was not operated continuously the values are only approximate.

TABLE II

MEASUREMENTS IN WHICH THE INITIAL SOLID PHASE WAS VANADIUM TETROXIDE

Time in hours	Temp., °C.	Rate of flow, cc. per min.	Inlet volumes cc. CO_2	Inlet volumes cc. CO	Outlet volume cc. CO	p_{CO_2}/p_{CO}
	756	18.38	539.4	12.0	0.046	1.2×10^4
4.0	747 ± 3	17.21	620.5	16.3	.089	7150
5.5	756	19.07	498.3	73.8	.089	6430
10.0	757	20.88	555.3	71.1	.884	707
12.0	741	17.07	491.7	71.6	2.267	248
15.0	751	17.02	498.0	12.6	0.960	530
18.0	751	16.56	478.5	18.3	1.602	309
19.5	749	16.54	483.0	13.2	1.847	267
21.5	753	17.34	520.2	0	1.158	448
24.5	755	17.12	513.6	0	1.064	482
26.0	752	16.95	508.5	0	1.032	492
30.0	754	17.34	508.8	11.4	1.655	313
	744	14.60	436.9	42.2	0.068	7100
	797	19.72	591.6	0	.087	6800
	793	17.80	521.4	42.6	.082	6900

The last three experiments of Table II were made after the sample had again been oxidized in air. Between the first and second and the second and third the new gas mixtures were allowed to flow approximately two and one half hours.

Discussion

The values of the ratio CO_2/CO measured over the samples which were largely vanadium trioxide present no great variations with the exception of the four values denoted by *c*. Just prior to the first of these measurements the sample had been reduced completely to vanadium trioxide. The explanation advanced by Taylor[10] to account for the analogous results with iron oxides reported by Richardson, Vibrans and Bell[11] appears sufficient to account for these results. Ten hours of heating at 890 to 900° were required before the ratio attained the approximately constant value near 140. On account of the small conversion of carbon dioxide to carbon monoxide it may well have required ten hours of heating to build up the vanadium tetroxide phase necessary for equilibrium by phase rule criteria. Evidently this stage had been passed before the first measurement of Table I was made.

Though very satisfactory results were obtained on reducing vanadium tetroxide when vanadium trioxide was the predominant solid phase (see Table I), the results obtained when the tetroxide predominated were erratic. The carbon dioxide–carbon monoxide ratios were at first much greater than those previously obtained, and though they dropped considerably after continued heating, they did not become constant at what we consider the normal equilibrium value. Except in this last respect these results were very similar to the ones obtained by Pease and Cook[12] in the reduction of nickelous oxide by hydrogen. A "surface effect," which was smaller in amount and of shorter duration, has also been observed by Emmett and Shultz[13] in the reduction of cobaltous oxide by carbon monoxide. In view of the fact that the vanadium tetroxide samples contained appreciable amounts of the trioxide from the first, it would appear that a "surface effect" rather than a lack of the required number of phases must be resorted to as an explanation. If one assumes that the difference in the reactions during the initial and later stages is due to the presence and participation of a more active vanadium tetroxide, one calculates as did Almquist,[14] from the average value of the ratio in the initial stages at 750°, 7100 and 380 in the later stages, V_2O_4 (active) = V_2O_4; $\Delta F = -5950$ cal., and from the last two values of Table II and an interpolation of Table I, for 795° $\Delta F = -6730$ cal. Thus the average energy per mole exceeded that of the stable oxide by about 6000 cal.

Table III summarizes the stable equilibrium measurements on Reaction 5 and presents values for Reaction 3 derived from Reaction 5 and the water-gas reaction.[15]

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(10) H. S. Taylor, *Chem. Met. Eng.*, **27**, 1263 (1923).

(11) A. S. Richardson, F. C. Vibrans and W. P. Bell, *Science*, **56**, 27 (1922).

(12) R. N. Pease and R. S. Cook, THIS JOURNAL, **48**, 1199 (1926).

(13) P. H. Emmett and J. F. Shultz, *ibid.*, **52**, 1782 (1930).

(14) J. A. Almquist, THIS JOURNAL, **48**, 2820 (1926).

(15) A. R. Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

TABLE III

EQUILIBRIUM OVER VANADIUM TRIOXIDE–VANADIUM TETROXIDE

Temperature, °C.	751	780	820	850	896
p_{CO_2}/p_{CO}	380	297	220	189	140
p_{H_2O}/p_{H_2}	296	258	219	207	176

Figure 1 represents the data on Reaction 5 and Fig. 2 the water vapor–hydrogen ratios over the various pairs of phases.

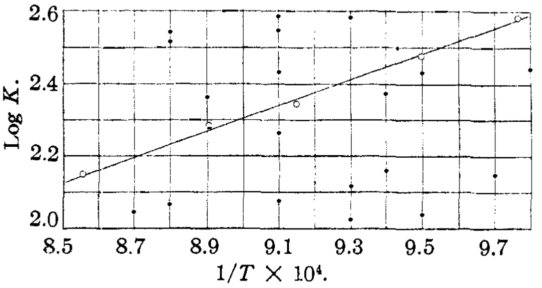

Fig. 1.

Over this temperature range Reaction 5 may be represented by

$$\log K = 3530/T - 0.8747$$

the average deviation in K being 1.5%. Though the equation involving the heat capacities is only slightly better in this range, it is to be preferred in extrapolating the data to other temperatures. Whereas heat capacity data for vanadium are now available, there are no data for the vanadium oxides; consequently Kopp's rule (*i. e.*, 4 cal. per gram atom of oxygen in the oxides) has been used for the solid phases. For the gases empirical equations fitted to values derived from spectroscopic data have been used.[16] Least square solutions of $\Sigma(= \Delta H_0/T + I)$ lead to

$$\Delta F^\circ = -15{,}467 + 3.9467\ T \ln T - 4.178 \times 10^{-3}\ T^2 + 5.422 \times 10^{-7}\ T^3 - 20.326\ T$$

and $\Delta F^\circ_{298.1} = -15{,}180$ and $\Delta H_{298.1} = -16{,}300$ cal.

Similar recalculations of Kobayashi's[2] results for Reactions 1 and 2 yield the equations

$$\Delta F^\circ = 60{,}146 + 3.7596\ T \ln T - 1.2866 \times 10^{-3}\ T^2 + 0.454 \times 10^{-7}\ T^3 - 42.503\ T$$

$$\Delta F^\circ = 32{,}625 + 3.7596\ T \ln T - 1.2866 \times 10^{-3}\ T^2 + 0.454 \times 10^{-7}\ T^3 - 35.675\ T$$

and $\Delta F^\circ_{298.1}$ for the two reactions equals 53,748 and 28,263 cal., respectively. Combination of these data with the free energies of formation of water vapor, carbon monoxide and carbon dioxide[17] leads to the following free energies of formation at 25°: vanadium dioxide, −216,510; vanadium trioxide, −299,280; and vanadium tetroxide, −345,850 cal.

From the ΔH of Reaction 5 and the heat of combustion of carbon monoxide,[18] $\Delta H_{298.1} = -67{,}623$ cal., for the reaction

$$V_2O_3 + {}^1/_2O_2 = V_2O_4;\ \Delta H_{298.1} = -51{,}323 \text{ cal.}$$

Mixter's[19] calorimetric value for this reaction, −59,600 cal., is the result of the mean of two widely varying determinations each, of sodium peroxide fusions of the two oxides. Accordingly as one takes the various pairs of individual values the results vary from −51,100 to −67,860 cal.

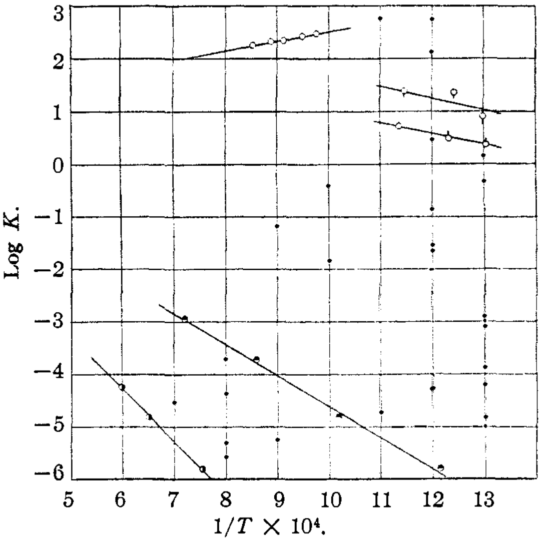

Fig. 2.—◑, V–V_2O_3, Kobayashi; ⊖, V_2O_2–V_2O_3, Kobayashi; ○, V_2O_3–V_2O_4, calculated from the CO_2–CO system; ♂, V_2O_3–V_2O_4, Müller; ♀, V_2O_4–V_2O_5, Müller.

Summary

Values of the equilibrium constant for the reaction $V_2O_4 + CO = V_2O_3 + CO_2$ have been determined over the temperature range 750 to 896° by a flow method. The solid phases were vanadium trioxide and vanadium tetroxide formed by oxidation of the trioxide with carbon dioxide. Most of the equilibrium measurements involved reduction of the solid phase.

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(16) H. M. Spencer and J. L. Justice, THIS JOURNAL, **56**, 2301 (1934). For equations of the form $C_p = a + bT + cT^2$, the constants are

	a	$b \times 10^3$	$c \times 10^7$
Carbon monoxide	6.3424	1.8363	− 2.801
Carbon dioxide	6.3957	10.1933	−35.333
Hydrogen	6.9469	−0.1999	4.808
Water vapor	7.18 73	2.3733	2.084

(17) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, pp. 607 and 608.

(18) F. D. Rossini, *Bur. Standards J. Research*, **6**, 37 (1931).

(19) W. G. Mixter, *Am. J. Sci.*, [4] **34**, 141 (1912).

Free energies and heats of formation have been calculated.

Attempts to measure the equilibrium constant, starting with vanadium tetroxide obtained by oxidation of the tetroxide in air, gave high values of the carbon dioxide–carbon monoxide ratio, which decreased with continued reduction. This "surface effect" is somewhat similar to that noted by other investigators.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, NO. 146]

Empirical Heat Capacity Equations for Simple Gases

BY HUGH M. SPENCER AND JOHN L. JUSTICE

The determination of the thermodynamic properties of the simple diatomic gases from the application of statistical mechanics to spectroscopic data by the accurate summation and approximation methods, in the hands of Giauque, Johnston, Gordon and others, has proved to be an important and powerful method. While for gaseous equilibria (and certain gas–solid equilibria where the solids have been investigated thoroughly to temperatures approaching the absolute zero) the results of these calculations may be used and tested directly without even the calculation of the heat capacities, the heat capacity data should be of great utility in the interpretation of many heterogeneous equilibria if they were available in the form of convenient empirical equations.

Some time ago, after these calculations were commenced, Bryant[1] published a series of equations fitted to values derived by the Planck–Einstein equation. In view of the insufficiencies of this equation for such gases as hydrogen, it has seemed worth while to present the equations based upon the more accurate calculations.

Table I presents the results of least square solutions of the data in the form, $C_p = a + bT + cT^2$, at even hundreds from 300 to 1500°K., which is a useful range for heterogeneous equilibria.

TABLE I

Substance	a	$b \times 10^3$	$c \times 10^7$	% deviation Max.	% deviation Av.	Source
H_2	6.9469	−0.1999	4.808	0.49	0.19	(2a)
O_2	6.0954	3.2533	−10.171	.57	.23	(2b)
Cl_2	7.5755	2.4244	− 9.650	1.13	.59	(2c)
Br_2	8.4228	0.9739	− 3.555	.71	.25	(2d)
N_2	6.4492	1.4125	− 0.807	1.35	.54	(2e)
CO	6.3424	1.8363	− 2.801	1.38	.47	(2e)
HCl	6.7319	0.4325	3.697	0.98	.48	(2c)
HBr	6.5776	0.9549	1.581	1.23	.54	(2d)
H_2O	7.1873	2.3733	2.084	1.05	.38	(2f)
CO_2	6.3957	10.1933	−35.333	2.17	.76	(2c)

The theoretical values for chlorine and hydrogen chloride were calculated by the method of Gordon and Barnes[3] and are for the equilibrium mixtures of the chlorine isotopes. The molecular constants given in Table II were derived from those of Elliott[4] and of Kemble[5] for $Cl^{35}Cl^{35}$ and HCl^{35}, respectively.

TABLE II

MOLECULAR CONSTANTS OF EQUILIBRIUM CHLORINE AND HYDROGEN CHLORIDE

	Chlorine	Hydrogen chloride
ω_e	561.2	2993.78
$x_e\omega_e$	3.9	53.56
B_e	0.2406	10.6041
α	0.0017	0.3279
ζ	0	0.01194
D_e	-1.768×10^{-7}	-5.326×10^{-4}
β	-3.0×10^{-9}	1.209×10^{-5}
F_v	-9.0×10^{-14}	1.46×10^{-8}

Since the complete treatment of carbon dioxide is not available at present, values were derived on the basis of a linear molecule with completely excited rotational energy, by means of the Planck–Einstein equation (actually derived by use of Table I of Reference 3), using the fundamental frequencies $\nu_2 = 667.5$, $\nu_1 = 1285$ and $\nu_3 = 2350.1$ cm.$^{-1}$,[6] the first of which is doubly degenerate. The theoretical values thus calculated are given in Table III ($R = 1.9869$ cal.).

The theoretical values derived by Gordon and Barnes[2d] for bromine and hydrogen bromide are equivalent to those for the equilibrium mixtures. For the latter this follows because the reduced masses of HBr^{79} and HBr^{81} are very nearly equal.

Attention may be called to two facts, namely, that the theoretical values are those of the gases

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