WATER VAPOUR EQUILIBRIA ON VANADIUM AND ITS OXIDES.

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Synopsis.

The oxidation-reduction equilibrium of vanadium has been investigated by the dynamical method of Wartenberg and Aoyama. By the experiment it has been suggested that the chemical changes take place in the two stages under the experimental conditions, and the reactions might be expressed by the following: $V+H_2O \rightleftarrows VO+H_2$ and $2VO+H_2O \rightleftarrows V_2O_3+H_2$. Thermodynamic calculations have been made for the above reactions, and the result of the calculated heats of formation agreed fairly well with that of the determinations made by other investigators.

Introduction.

A reduction equilibrium on chromic oxide was determined by H. v. Wartenberg and S. Aoyama⁽¹⁾ in 1927. The principle applied by these investigators consisted of passing a stream of hydrogen saturated with water vapour of known partial pressure on metallic chromium and the oxidation equilibrium is measured at various temperatures by observing the change in colour which takes place on the surface of the metal due to the process of oxidation and reduction going on by the small quantity of oxygen. Later in 1932, by applying the same principle S. Aoyama and Y. Oka⁽²⁾ determined the oxidation-reduction equilibrium of manganese, in distilled state. Since vanadium is a very refractory substance, and is hardly reducible like the metals mentioned above, and its oxide is reducible by hydrogen only when the latter is carefully dried⁽³⁾, it has been attempted by the present writer to measure the oxidation equilibrium of vanadium by the principle described above.

Experimental.

Apparatus. The apparatus used was quite the same as described by Wartenberg and Aoyama in their paper, except the reaction tube and the pump for circulating gas. Instead of a silica-tube, a pyrex glass-tube,

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(1) *Z. Elektrochem.*, **33** (1927), 144.
(2) *Nippon Kagaku-kaishi* (*J. Chem. Soc. Japan*), **53** (1932), 417.
(3) H. v. Wartenberg, J. Broy & R. Reinicke. *Z. Elektrochem.*, **29** (1923), 214.

5 cm. in diameter and 50 cm. in length, was used as the reaction tube (Fig. 1). To the lower end of the pyrex tube was attached a glass cap with a side tube for introducing hydrogen having a rubber stopper which is overlaid with mercury, and through which two insulated copper leading rods, each 3 mm. in thickness, were thrust into the pyrex tube. The joint between the pyrex tube and the glass cap was made tight with picein. A small hole was made at the top of each copper rod to which was inserted each end of molybdenum spiral, of the furnace which is 25 mm. in length, 1 cm. in diameter and 18 turns of the spiral. (Two molybdenum wires each 0.4 mm. in diameter were twisted in making the furnace). On the top of the pyrex tube a glass cap was placed having

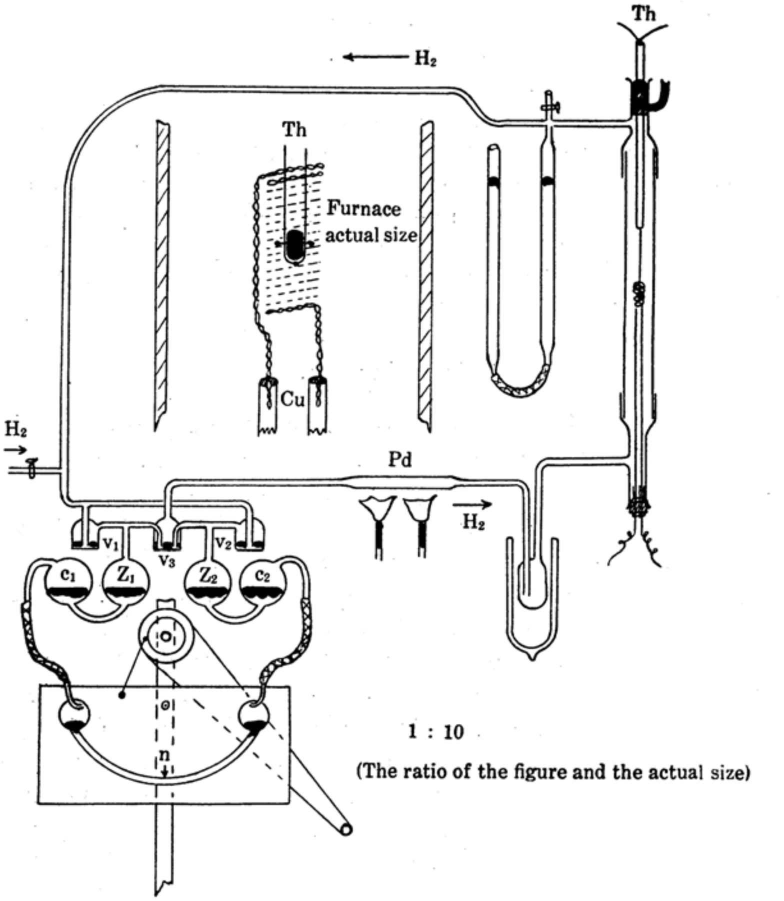

Fig. 1.

an exit tube for hydrogen and also a hanger for a piece of metallic vanadium (3×4×5 mm.). A thermocouple was fused in a glass tube, which is movable through two cork stoppers and is made gas tight with mercury seal. The piece of the metallic vanadium was bound with Pt-wire directly at the junction of the couple.

The pump for circulating gas used in this experiment was a modified form of mercury pump devised by K. Scheel and W. Heuse⁽⁴⁾, and had been constructed by Dr. S. Aoyama for his recent experiment on manganese. The mercury pump which has been kindly lent by Dr. Aoyama consists of two glass bulbs Z_1 and Z_2, in which mercury is filled and emptied, alternately, by the pressure due to contraction and expansion of air of constant volume in the communicating bulbs c_1 and c_2. The contraction and expansion of the air are caused by the alternating lateral motion (effected by a motor) of glass tube n, which is half filled with mercury and each end of which is connected to the communicating bulbs with rubber tubes; the mercury in n remains almost stationary even while n moves. If, for example, n inclines to the right, the air in c_1 expands resulting the mercury in Z_1 to be emptied and filling the mercury in c_1. Due to the depression of mercury in Z_1 hydrogen is inhaled through mercury valve v_1; when n inclines to the left the hydrogen is puffed off through mercury valve v_3. Hydrogen passes then over Pd-asbestos heated at about 200°C., and then through the trap dipped in a Dewar's beaker into the pyrex tube and from here returns again to Pd-asbestos through the pump, with a current velocity of about 200 c.c. per minute. The communicating tube of mercury serves to keep the pressure in the closed system at one atmospheric pressure when the furnace is heated at high temperatures.

The furnace was heated by an electric current; a temperature of 1300°C. has been obtained by a current of 18 amperes at 24 volts:

Bath. The temperatures of the bath applied were:

–78.5°C. (carbon dioxide-alcohol),
–19.5°C. (sodium chloride-ice mixtures),
–37.0°C. (melting mercury) } frozen by pouring liquid air drop by drop on mercury
–47.0°C. (solid mercury) } and kept it constant temperature within ±0.3°C. by
–57.0°C. („) } hand regulation,

corresponding respectively to $p_{H_2O} = 6.65 \cdot 10^{-7}$ atm. press.⁽⁵⁾; $1.07 \cdot 10^{-3}$, $1.76 \cdot 10^{-4}$, $5.53 \cdot 10^{-5}$, $1.45 \cdot 10^{-5}$ atm. press.⁽⁶⁾

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(4) *Ann. Phys.*, **40** (1913), 474.
(5) Vapour pressure of H_2O, Daudt, *Z. Physik. Chem.*, **106** (1923), 263.
(6) „ „ „ Landolt Börnstein Roth/Scheel, Hw., II, 1315.

Material. The vanadium was prepared by the Goldschmidt method, using 100 parts V_2O_5, 40 parts Al, and 12 parts Na_2CO_3 as flux(7) in an alundum crucible lined with pure magnesia, and the chemical analysis indicates:

Slag (mainly Al_2O_3)	V	Al	Fe
1.4	97.0	1.5	0.4

Results.

Preliminary Experiments. By the use of the apparatus described above some preliminary experiments were carried out as to see whether vanadium metal could be distinguished merely by its appearance from its oxide that has been produced when the metal was heated at various temperatures in an atmosphere of hydrogen saturated with water vapour of very small partial pressure. In the first experiment, the temperature of the bath was kept at –19.5°C. (sodium chloride-ice mixtures), and vanadium was heated at 1000°C. for 2 hours. After cooling it was found that the silver-white metallic surface altered to black. As the temperature of the furnace was then raised to 1050°C. and maintained at this temperature for half an hour, the colour of the metallic surface became darker. After the temperature was raised to and maintained at 1150°C. for an hour, it was found that the colour faded to grey. Then, it was again heated at the same temperature for an another hour, but no change in colour was noticed. In spite of the fact that the heating temperature was further raised about every 100°C. up to 1550°C., and the time for maintaining each temperature was set to about 3 hours, it still remained grey; thus an attempt to reduce the metal to its initial condition was proved unsuccessful, since it was found experimentally difficult to maintain the heating for so many hours at such an elevated temperature as above 1550°C. In the second experiment, the temperature of the bath was lowered and kept at –78.5°C. (carbon dioxide-alcohol), and a different piece of vanadium metal was heated at 1400°C. for an hour and a half. This time no physical change has been observed upon the metal. The temperature was then lowered to 1000°C. and maintained at this temperature for a quarter of an hour. During this time the colour of the surface changed to faint grey. The temperature was, therefore, again raised to 1100°C., and after being maintained at this temperature for an hour, it was reduced to its original condition. When the metal was heated at 900°C. for half an hour, it was again tinged with grey. The colour

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(7) M. Oya, *Sci. Rep., Tohoku Imp. Univ., Japan*, **19** (1930), 236.

was still unchanged after the heating had been continued for further 3 hours under the same temperature. In order to see whether it would be darkened in colour at the lower temperatures, as might have been expected from the above first preliminary experiment, the temperature was lowered about 100°C. at a time. At 600°C. it remained grey, in spite of the fact that the heating had been continued for 20 hours; while after 20 hours' heating at 500°C., it was recognized undoubtedly that the grey colour changed to black.

It will be obvious from the above experiments that there must be two different forms of vanadium oxides under the present experimental conditions. It can be stated that they are in equilibrium with each other, besides vanadium with the lower oxide. It is also found that the equilibrium temperatures of carbon dioxide-alcohol bath (–78.5°C.) are between 500 and 600°C. and also 1000 and 1100°C.

Among the following well known vanadium oxides⁽⁸⁾, VO (or V_2O_2), V_2O_3, V_2O_4 and V_2O_5, the last two are easily reduced to V_2O_3 by dry hydrogen⁽⁹⁾, and, moreover, according to H. Müller⁽¹⁰⁾ the values of $K = p_{H_2O} / p_{H_2}$ in the V_2O_4 / V_2O_3-reaction, $V_2O_3 + H_2O \rightleftarrows V_2O_4 + H_2$, are to be 2.20–5.03 over the range of temperature 493–606°C, and the values of K in the V_2O_5 / V_2O_4-reaction, $V_2O_4 + H_2O \rightleftarrows V_2O_5 + H_2$, are to be 7.6–23.3 over the range of temperature 496–600°C. In the present experiment the values of $K = p_{H_2O} / p_{H_2} = p_{H_2O} / 1 = 10^{-7} \sim 10^{-3}$ as it has been described above. Therefore, under the present experimental conditions these oxides are considered to be out of question, and it is assumed that the reactions may be expressed by (I) and (II), as follows:

$$\text{(I)} \quad V + H_2O \rightleftarrows VO + H_2 \qquad \text{and}$$

$$\text{(II)} \quad 2VO + H_2O \rightleftarrows V_2O_3 + H_2 .$$

This must yet be confirmed by the calculation of thermal values of the reactions. This calculation will be described subsequently.

Final Experiments. Now then, the equilibrium temperatures of both reactions were measured at the bath temperatures mentioned above. Each equilibrium temperature of oxidation and reduction was obtained as the mean of adjacent temperatures within about 20°C.

The results are shown in Tables 1 and 2. The experimental results are best detected by the fact that in each reaction the relation between

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(8) J. W. Mellor, *Comp. Treat. Inorg. Chem.*, **9** (1929), 739.

(9) cf. (8) p. 741, 744.

(10) W. Biltz's Festschrift, Hannover (1927); cf. (8) p. 741, 744.

Table 1.

$V+H_2O \rightleftarrows VO+H_2$;

(i) Bath –78.5°C.

Thermoelec. force millivolts	Initial colour of V	Result	Concluded to be
10.7	silver-white	after 4 hrs. grey	oxidation
11.8	grey	,, 2 ,, silver-white	reduction
11.0	faint grey	,, 5 ,, grey	oxidation
11.2	grey	,, 3 ,, silver-white	reduction

Equilibrium temperature between 11.0 and 11.2 = 11.1 millivolts = 1052°C.

(ii) Bath –57.0°C.

12.8	faint grey	after 2 hrs. grey	oxidation
14.2	grey	,, 3 ,, silver-white	reduction
14.0	silver-white	,, 4 ,, grey	oxidation
14.9	grey	,, 1.5,, silver-white	reduction

Equilibrium temperature between 14.0 and 14.2 = 14.1 millivolts = 1268°C.

(iii) Bath –47.0°C.

15.6	silver-white	after 3.5 hrs. grey	oxidation
16.7	grey	,, 1 ,, silver-white	reduction
15.9	silver-white	,, 1 ,, grey	oxidation
16.1	grey	,, 2 ,, silver-white	reduction

Equilibrium temperature between 15.9 and 16.1 = 16.0 millivolts = 1397°C.

$$2\,VO + H_2O \rightleftarrows V_2O_3 + H_2;$$

(i) Bath –78.5°C.

Thermoelec. force millivolts	Initial colour of V	Result	Concluded to be
4.6	faint grey	after 6 hrs. grey	
4.9		,, 18 ,, black	oxidation
5.5	black	,, 20 ,, grey	reduction
4.4	grey	,, 20 ,, black	oxidation
5.1	black	,, 24 ,, grey	reduction

Equilibrium temperature between 4.9 and 5.1 = 5.0 millivolts = 550°C.

(ii) Bath –57.0°C.

6.7	grey	after 2.5 hrs. black	oxidation
7.3	black	,, 1.5 ,, grey	reduction
6.5	grey	,, 3 ,, black	oxidation
6.9	black	,, 2 ,, grey	reduction

Equilibrium temperature between 6.7 and 6.9 = 6.8 millivolts = 710°C.

(iii) Bath –37.0°C.

8.5	grey	after 1¼ hrs. black	
8.8		,, 1 ,, more black	oxidation
9.4	black	,, ½ ,, grey	reduction
9.1	,,	,, 1.5 ,, grey	,,
8.9	grey	,, 2 ,, black	oxidation

Equilibrium temperature between 8.9 and 9.1 = 9.0 millivolts = 890°C.

(iv) Bath –19.5°C.

11.8	grey	after 2 hrs. black	oxidation
12.8	black	,, 1 ,, grey	reduction
12.4	,,	,, 2 ,, grey	,,
12.0	,,	,, 3 ,, grey	,,

Equilibrium temperature between 11.8 and 12.0 = 11.9 millivolts = 1112°C.

Table 2.

a) $Kp._1$-values and equilibrium temps. for V/VO.

Bath (°C)	$K_{p\cdot1}$	log $K_{p\cdot1}$	Temp. C°	T	$1/T$
−78.5	$6.65\cdot10^{-7}$	−6.1772	1052	1325	0.0007547
−57.0	$1.45\cdot10^{-5}$	−4.8394	1268	1541	6489
−47.0	$5.53\cdot10^{-5}$	−4.2576	1397	1670	5988

b) $Kp._2$-values and equilibrium temps. for VO/V_2O_3.

Bath (°C)	$K_{p\cdot2}$	log $K_{p\cdot2}$	Temp. C°	T	$1/T$
−78.5	$6.65\cdot10^{-7}$	−6.1772	550	823	0.0012150
−57.0	$1.45\cdot10^{-5}$	−4.8394	710	983	10172
−37.0	$1.76\cdot10^{-4}$	−3.7537	890	1163	08598
−19.5	$1.07\cdot10^{-3}$	−2.9723	1112	1385	07220

the logarithms of equilibrium constants (log $K_p = p_{H_2O}/p_{H_2}$) and the reciprocals of absolute temperatures (1/T) is indicated by a straight line (Fig. 2, they are analogous with those in W/WO_2 and WO_2/W_2O_5)⁽¹¹⁾. Consequently, they can be expressed by the general equation of first order of the reaction isochore

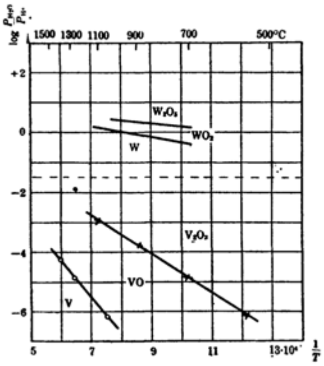

Fig. 2.

$$\log K_p = -\frac{Q}{4.571\,T} + C.$$

Thermodynamical Calculations.

From the values given in the above Table 2a) and b) the following empirical equations for straight lines can be derived:

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(11) L. Wöhler & R. Günther, *Z. Elektrochem.*, **29** (1923), 276;
L. Wöhler, Z. Shibata & R. Kunst, *Z. Elektrochem.*, **38** (1932), 808.

$$\mathrm{V/VO}: \quad \log K_{p\cdot 1} = -\frac{12333}{T} + 3.141$$

$$\mathrm{VO/V_2O_3}: \quad \log K_{p\cdot 2} = -\frac{6482}{T} + 1.747.$$

By the equation $\log K_p = -\frac{Q}{4.571\,T} + C$, in which $-\frac{Q}{4.571} = tg\,\alpha$ in the equation of first order, it follows that Q'_1 and Q'_2, the heat of the reactions (I) and (II), are obtained as the product of -4.571 with -12333 and -6482, respectively: that is,

$$\mathrm{V + H_2O = VO + H_2} + Q_1'(= 56.4 \text{ Cal.})$$

$$\mathrm{2VO + H_2O = V_2O_3 + H_2} + Q_2'(= 29.6 \text{ Cal.})$$

By combining the above empirical equations with the equation for dissociation of water vapour, the dissociation pressures of the vanadium oxides can be calculated;

$$K'_{p_{\mathrm{H_2O}}} = \frac{p^2_{\mathrm{H_2}} \cdot p_{\mathrm{O_2}}}{p^2_{\mathrm{H_2O}}} = \frac{1 \cdot p_{\mathrm{O_2}}}{K_p^2}, \quad \text{thus} \quad p_{\mathrm{O_2}} = K'_{p_{\mathrm{H_2O}}} \cdot K_p^2 .$$

$$\text{(III)} \quad \mathrm{2VO \rightleftarrows 2V + O_2} + Q_1;$$

$$\mathrm{O_2}\text{-pressure} \quad = p_1 = K'_{p_{\mathrm{H_2O}}} \cdot K^2_{p\cdot 1},$$

$$\text{(IV)} \quad \mathrm{2V_2O_3 \rightleftarrows 4VO + O_2} + Q_2;$$

$$\mathrm{O_2}\text{-pressure} \quad = p_2 = K'_{p_{\mathrm{H_2O}}} \cdot K^2_{p\cdot 2} .$$

By applying equation for dissociation of water⁽¹¹⁾ which, although approximate, is useful, $\log K'_{p_{\mathrm{H_2O}}} = -\frac{26000}{T} + 6.06$, we obtain

$$\log p_1 = -\frac{26000}{T} + 6.06 + 2\left(-\frac{12333}{T} + 3.141\right)$$

$$= -\frac{50666}{T} + 12.342 \quad \text{atm. press.}$$

and similarly

$$\log p_2 = -\frac{38964}{T} + 9.554 \quad \text{atm. press.}$$

By the most general form of equation for vapour pressure, $\log p = -\frac{Q}{4.571T} + C$, approximate heat tonings Q_1 and Q_2 of the reactions (III) and (IV) can be calculated. That is,

$$Q_1 = -50666 \cdot -4.571 = 231.6 \text{ Cal.}$$

$$Q_2 = -38964 \cdot -4.571 = 178.1 \text{ Cal.}$$

or, the heat of the reactions:

$$2V + O_2 = V_2O_2 + Q_1 \ (= 231.6 \text{ Cal.})$$

$$V_2O_2 + 1/2\, O_2 = V_2O_3 + 1/2\, Q_2 \ (= 89.0 \text{ Cal.})$$

and by addition

$$2V + 3/2\, O_2 = V_2O_3 + Q_3 \ (= Q_1 + 1/2\, Q_2 = 320.6 \text{ Cal.})$$

Although the approximate value of heat of oxidation Q_1 of vanadium to its dioxide is little higher than that calculated by R. E. Slade & G. I. Higson(12) and that determined by W. G. Mixter, it was very close to their values. Heat of oxidation Q_3 of vanadium to its trioxide is found between those determined by Mixter and O. Ruff & L. Friedrich(13); but of the two it was closer to that of Ruff & Friedrich. The values obtained by the author and the others mentioned above are given below for comparison:

	Author	Mixter	Ruff and Friedrich	Slade and Higson
Q_1	231.6	greater than 209(14)	—	222.0
Q_3	320.6	,, 353(15)	302±10	—

Since the values obtained closely agree with the others, it becomes obvious that the equilibria dealing here are correct, that is to say, the following reactions will undoubtedly take place,

$$V + H_2O \rightleftarrows VO + H_2$$

and

$$2VO + H_2O \rightleftarrows V_2O_3 + H_2 .$$

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(12) *J. Chem. Soc.*, **115** (1919), 205.

(13) *Z. anorg. Chem.*, **89** (1914), 279.

(14) and (15) Calcd. according to Mixter's data; *Sill. Journ.* **34** (1912), 148; *Z. anorg. Chem.*, **78** (1912), 221.

Further, by applying Siegel's exact equation⁽¹⁶⁾ for dissociation of water vapour, $[\log K_c = \frac{-24900}{T} + 1.335 \log T - 9.65 \cdot 10^{-5}\, T + 1.37 \cdot 10^{-7}\, T^2 - 6.65 \cdot 10^{-11}\, T^3 + 1.907 \cdot 10^{-18}\, T^5 - 1.08]$ the dissociation pressures of the two oxides at various temperatures are calculated as follows:

O_2-pressure at atmospheric.

abs. temp.	$p_1(V/VO)$	$p_2(VO/V_2O_3)$
823	—	$2.47 \cdot 10^{-37}$
983	—	$1.49 \cdot 10^{-29}$
1163	—	$2.69 \cdot 10^{-23}$
1325	$2.13 \cdot 10^{-25}$	—
1385	—	$3.94 \cdot 10^{-18}$
1541	$5.97 \cdot 10^{-20}$	—
1670	$1.80 \cdot 10^{-17}$	—
3610	—	1.0
3720	1.0	—

It will be noticed from the table that the oxygen pressure of trioxide will be one atmosphere at about 3610° abs., and that of dioxide at about 3720° abs.

The Free Energy and Heat of Formation of VO. Using the following heat capacities of substances

$$\begin{aligned} &\text{for VO};\quad C_p = 10.2^{(17)} \\ &\text{,, } H_2;\quad C_p = 6.50 + 0.0009\, T^{(18)} \\ &\text{,, V};\quad C_p = 6.2^{(17)} \\ &\text{,, } H_2O\,(g);\quad C_p = 8.81 - 0.0019\, T + 0.00000222\, T^{(18)} \end{aligned}$$

being involved in the reaction,

$$V + H_2O = VO + H_2\,,$$

the general equation for heat of formation and free energy equation can be given as follows:

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(16) W. Siegel, *Z. Physik. Chem.*, **87** (1914), 641.

(17) Calcd. by Kopp's rule; cf. Noyes & Sherrill, "Chem. Principle," (1930), 93.

(18) Lewis & Randall, "Thermodynamics," (1923), 80.

$$\text{(A)}\qquad \varDelta H = \varDelta H_0 + 1.69\,T + 0.0014\,T^2 - 0.00000074\,T^3$$

$$\text{(B)}\qquad \frac{\varDelta F^0}{T} = \frac{\varDelta H_0}{T} - 1.69\ln T - 0.0014\,T + 0.00000037\,T^2 + I\,.$$

In the latter equation the values of $\varDelta H_0$ and I are obtained by an application of the relation

$$\varDelta F^0 = -RT\ln K_p\,,$$

in which the values of K_p are known, as shown in Table 2 a),

$$\varDelta H_0 = -59526 \text{ cal}, \quad I = 30.09$$

Substituting these values in (A) and (B),

$$\varDelta H = -59526 + 1.69\,T + 0.0014\,T^2 - 0.00000074\,T^3$$

$$\frac{\varDelta F^0}{T} = \frac{-59526}{T} - 1.69\ln T - 0.0014\,T + 0.00000037\,T^2 + 30.09\,.$$

Solving for T at 298°, we find

$$\varDelta F^0_{298} = -53543 \text{ cal}, \quad \varDelta H_{298} = -58918 \text{ cal},$$

Combining the values of $\varDelta F^0_{298} = -54507$, cal⁽¹⁹⁾ and $\varDelta H_{298} = -57820$ cal⁽²⁰⁾ for the free energy and heat of formation of water vapour from its element, the free energy and heat of formation of VO from its element can be calculated as follows:

$$\begin{array}{lll} V + H_2O = VO + H_2 & ; \ \varDelta F^0_{298} = -53543 \text{ cal}, & \varDelta H_{298} = -58918 \text{ cal.} \\ H_2 + 1/2\,O_2 = H_2O(g) & ; \ \varDelta F^0_{298} = -54507 \text{ cal}, & \varDelta H_{298} = -57820 \text{ cal.} \\ \text{hence}\ V + 1/2\,O_2 = VO & ; \ \varDelta F^0_{298} = -108050 \text{ cal}, & \varDelta H_{298} = -116738 \text{ cal.} \\ \text{or (i)}\ 2V + O_2 = V_2O_2 & ; \ \varDelta F^0_{298} = -216100 \text{ cal}, & \varDelta H_{298} = -233476 \text{ cal.} \end{array}$$

The final value –233476 cal, the heat of formation of V_2O_2 from its element, is nearly equivalent to the approximate value $Q_1 = 231.6$ Cal, for the corresponding heat of formation already obtained, in which it has been calculated by neglecting the change in heat capacities with temperature.

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(19) Lewis & Randall, "Thermodynamics," (1923) p. 485.

(20) ibid. p. 477.

The Free Energy and Heat of Formation of V_2O_3. In the same manner as in the preceding section the general equations for heat of formation and also for free energy are derived for the reaction

$$2VO + H_2O = V_2O_3 + H_2\,;$$

From the heat capacities of these substances:

$$\begin{aligned}
&V_2O_3 &&;\quad C_p = 24.4^{(17)}\\
&H_2 &&;\quad C_p = 6.50 + 0.0009\,T\\
&2VO &&;\quad C_p = 20.4^{(17)}\\
&H_2O\,(g) &&;\quad C_p = 8.81 - 0.0019\,T + 0.00000222\,T^2\,,
\end{aligned}$$

are derived

$$\Delta H = \Delta H_0 + 1.69\,T + 0.0014\,T^2 - 0.00000074\,T^3$$

$$\frac{\Delta F^0}{T} = \frac{\Delta H_0}{T} - 1.69 \ln T - 0.0014\,T + 0.00000037\,T^2 + I\,.$$

Solving, we find

$$\Delta H_0 = -32124 \text{ cal.} \quad I = 23.22\,,$$

we may write,

$$\Delta H = -32124 + 1.69\,T + 0.0014\,T^2 - 0.00000074\,T^3$$

$$\frac{\Delta F^0}{T} = \frac{-32124}{T} - 1.69 \ln T - 0.0014\,T + 0.00000037\,T^2 + 23.22\,.$$

Hence

$$2VO + H_2O = V_2O_3 + H_2\,;\quad \Delta F^0_{298} = -28189 \text{ cal},\quad \Delta H_{298} = -31516 \text{ cal.}$$

$$H_2 + 1/2\,O_2 = H_2O\,(g)\quad;\quad \Delta F^0_{298} = -54507 \text{ cal},\quad \Delta H_{298} = -57820 \text{ cal.}$$

hence

$$\text{(ii)}\qquad 2VO + 1/2\,O_2 = V_2O_3\quad;\quad \Delta F^0_{298} = -82696 \text{ cal},\quad \Delta H_{298} = -89336 \text{ cal.}$$

The final value –89336 cal, the heat of formation of V_2O_3 from VO and oxygen is equal to the approximate value $Q_2/2 = 89.0$ Cal, for the corresponding heat of formation already described.

Lastly, from the values (i) and (ii) are calculated the free energy and heat of formation of V_2O_3 from its element:

$$2VO+1/2\,O_2=V_2O_3\ ;\quad \Delta F^0_{298}=-82696\ \text{cal},\quad \Delta H_{298}=-89336\ \text{cal}.$$

$$2V+O_2=2VO\quad ;\quad \Delta F^0_{298}=-216100\ \text{cal},\quad \Delta H_{298}=-233476\ \text{cal}.$$

hence

$$2V+3/2\,O_2=V_2O_3\quad ;\quad \Delta F^0_{298}=-298796\ \text{cal},\quad \Delta H_{298}=-322812\ \text{cal}.$$

This final value, –322812 cal, the heat of formation of V_2O_3 from its element is also nearly equal to the approximate value $Q_3=320.6$ Cal, for the corresponding heat of formation already obtained.

In conclusion the writer wishes to express his sincere thanks to Prof. Dr. Keizô Iwasé, under whose guidance this work has been carried out and also to Dr. Shin-ichi Aoyama for his kind advice he has extended in carrying out this work.

Summary.

1. The vanadium-water vapour equilibria on the phase V/VO and VO/V_2O_3 have been determined over the range $p_{H_2O}=1.07\cdot10^{-3}$ to $6.65\cdot10^{-7}$ atmospheric pressure by the method of H. v. Wartenberg and S. Aoyama.

2. From the measured equilibrium temperatures and the corresponding K_p-values, it has been derived the general equations of the reaction isochore $\log K_p=-\dfrac{Q}{4.571\,T}+C$ for the two systems:

$$\text{V/VO}\quad ;\quad \log K_{p\cdot1}=-12333/T+3.141$$

$$\text{VO/V}_2\text{O}_3\ ;\quad \log K_{p\cdot2}=-6482/T+1.747\ ,$$

and from these the approximate heat of reaction have been calculated:

$$V+H_2O=VO+H_2+Q'_1(=56.4\ \text{Cal.})$$

$$2VO+H_2O=V_2O_3+H_2+Q'_2(=29.6\ \text{Cal.})$$

3. Combining the above equations with the equation for dissociation of water vapour, the general equations for dissociation of vanadium oxides have been derived, and from these it has been calculated O_2-pressures for several temperatures and approximate values for the heat of formation of VO from V, of V_2O_3 from VO, and of V_2O_3 from V:

$$2V+O_2=V_2O_2+231.6\ \text{Cal.}$$

$$2VO+1/2\,O_2=V_2O_3+89.0\ \text{Cal.}$$

$$2V+3/2\,O_2=V_2O_3+320.6\ \text{Cal.}$$

4. By the use of the equations for heat capacities of substances being involved in each reaction, the free energies and heats of formation have been calculated at 25°C.; that of VO from its element and that of V_2O_3 from its element and also from VO and oxygen:

$$2V+O_2=V_2O_2 \quad ; \quad \Delta F^0_{298}=-216100 \text{ cal}, \quad \Delta H_{298}=-233476 \text{ cal}.$$

$$2VO+1/2\,O_2=V_2O_3 ; \quad \Delta F^0_{298}=-82696 \text{ cal}, \quad \Delta H_{298}=-89336 \text{ cal}.$$

$$2V+3/2\,O_2=V_2O_3 \quad ; \quad \Delta F^0_{298}=-298796 \text{ cal}, \quad \Delta H_{298}=-322812 \text{ cal}.$$

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