

# The Dissociation Pressure of VC at High Temperature and the Thermodynamic Properties

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The dissociation pressure of gaseous vanadium in the reaction  $VC(s) = V(g) + C(\text{graphite})$  has been determined in the range of 2346~2545°K by means of Knudsen cell effusion method.

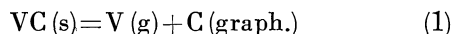
The pressure at the above temperature range is adequately expressed by  $\log P_v(\text{atm}) = -30,400/T + 7.50$ , from which, and coupling with the reported heat capacity data, the pertinent thermodynamic properties are calculated.

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## I. Introduction

Vanadium carbide plays an important role in alloy steels and refractory hard metals with the other transition metal carbides so that the study of its thermodynamic properties would contribute a great deal in understanding the character of those materials. The published data on the properties are, however, uncertain. Slade and Higson<sup>(1)</sup> have investigated the equilibrium reaction  $VO(s) + VC(s) = 2V(s) + CO$  and obtained the free energy change at a single temperature by measuring the partial pressure of CO gas. However, the fact that VO has a great solubility in VC suggests the equilibrium study of the above system is not reliable in determining the heat of formation of VC.<sup>(2)</sup>

The purpose of this investigation is to determine the dissociation pressure of vanadium atomic gas at high temperatures in the following reaction



It has been known that most of transition metal carbides of group IV, V and VI in the periodic table dissociate into monoatomic gas and graphite at high temperature.<sup>(3)</sup>

In this experiment it is also proved the dissociation of VC takes place in this fashion by means of indirect methods which will be described later. From the equilibrium constant  $K = P_V$  for the reaction at various temperatures, the pertinent thermodynamic properties of VC have been obtained from the following relationship:

$$\Delta F^\circ = -RT \ln P_V = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

If the pressure outside the Knudsen cell is sufficiently low in comparison to the vapor pressure of metal inside, the effusion of metal vapor in the free space of the cell occurs through an orifice without any disturbance and the probability of the atoms returning to the cell is negligibly small. Actually even if the outside of the cell is kept in high vacuum and the vapors effuse out continuously from an orifice, it is possible to keep the vapor

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(1) R. E. Slade and G. I. Higson: J. Chem. Soc., 115(1919), 205.

(2) H. Krainer and K. Kenopicky: Berg -u. Hüttenmänn Mh., 92 (1947), 166.

(3) W.A. Chupka, J. Berkowitz, C. F. Giese and M.G. Inghram: J. Phys. Chem., 62 (1958), 611.

inside the Knudsen cell in equilibrium with solid powder which provides it from the sufficient surface area. In order to obtain a sufficient weight loss for minimizing errors, it is desirable to make the orifice as large as possible within the limitation that the orifice diameter is less than the mean free path of the effusing gas. It is, in general, preferable to make the cell as small as possible in order to maintain a uniform temperature, but not too small so that the exposed area of the carbide powder would have a sufficient area for the attainment of equilibrium conditions in the cell.

The principles of the effusion method for the determination of vapor pressures have been presented elsewhere in detail.<sup>(4)</sup> Briefly it may be summarized by means of

$$P = \frac{W}{kat} \sqrt{\frac{2\pi RT}{M}} \quad (3)$$

where  $W$  is the weight loss in grams from a cell with an orifice smaller than  $1/10$ th of the mean free path of the effusing vapor;  $a$ , the orifice area in  $\text{cm}^2$ ;  $t$ , time in seconds;  $R$ , the ideal gas constant;  $T$ , the absolute temperature in  $^\circ\text{K}$ ;  $M$ , molecular weight of the vapor;  $P$ , the pressure in dynes/ $\text{cm}^2$ ;  $k$ , a correction factor due to the orifice structure, so called Clausing factor.

## 2. Experimental Method

**Material:** Vanadium carbide was prepared by melting metallic vanadium of 99.9% purity in a pure graphite crucible and kept at  $2400^\circ\text{C}$  for more than 10 hours. Combined carbon content of this material was 18.89% and possible impurities were Fe 0.04%, O 0.02% and free carbon 0.1% which will not disturb this equilibrium experiment. Lattice parameter was  $4.160 \pm 0.002 \text{ \AA}$ .

**Crucible:** Highest density graphite available was used for making the Knudsen cell shown in Fig. 1.

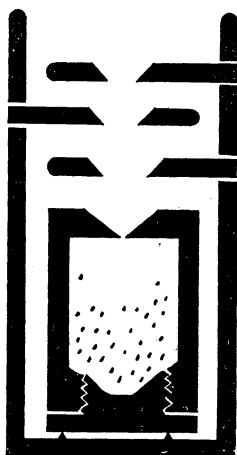


Fig. 1 Knudsen cell, and outer graphite crucible with baffles.

The cell was  $1 \sim 1/2$  inches high and 1 inch in diameter, fitted with a precision machined and threaded tight plug in the bottom. The orifice pierced by a drill,

the area of which was measured by utilizing a microscope.

**Temperature Measurement:** Measurement of temperature was made by means of a Leeds and Northrup optical pyrometer calibrated by observing the melting point of pure Pt wire under black body conditions. The observed temperature was corrected by means of the experimental relation well known  $1/T_{\text{obs.}} - 1/T_{\text{true}} = \text{constant}$ . Temperature measurements were accurate well within  $\pm 10^\circ\text{C}$ .

**Procedures:** Powdered VC was placed in a graphite cell and the plug was screwed on very tightly. The cell was then inserted in the outer crucible made of graphite and baffles were replaced as shown in Fig. 1. This assembly was then packed in the transparent quartz tube (D) with 40~48 mesh graphite powder as shown in Fig. 2. High vacuum

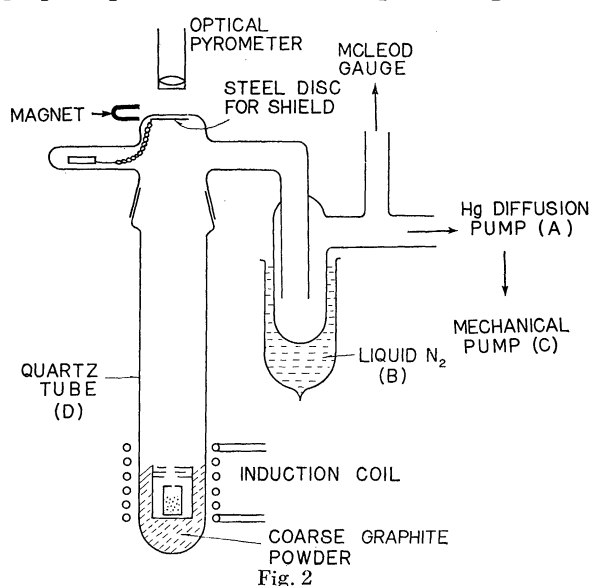


Fig. 2

better than  $5 \times 10^{-6}$  mmHg was obtained during each run by means of a mercury diffusion pump (A) and a liquid  $\text{N}_2$  trap (B) backed up with a Cenco Hyvac pump (C). The graphite parts were heated by means of an induction unit. After the cell had been maintained at a desired temperature for several hours, it was cooled. When the temperature of the cell was down to the room temperature, purified argon gas was admitted to break the vacuum. This procedure permitted degassing of the graphite cell and its contents. The cell was removed, and weighed accurately, placed again in the furnace, and heated to a desired temperature, held there for 6~10 hours that gives a sufficient weight loss, cooled rapidly and then reweighed. The total weight loss of the cell before and after each run is due to (a) the vaporization of graphite, (b) effusion of vanadium through the pores and (c) effusion of vanadium through the orifice. The first loss was determined with an empty cell, the second with a cell containing VC but having no orifice, the third was obtained by the difference between the weight losses for the cells with and without an orifice, but containing VC powder. The weight loss through the orifice was then used to calculate the dissociation pressure of gaseous vanadium from Eq. 3.

(4) M. Knudsen: *Kinetic Theory of Gases*, Methuen Ltd, London, (1934); *Vacuum Metallurgy*: Am. Electrochem. Soc., (1955).

### 3. Results and Discussion

It is important in treating data of this experiment to prove vanadium carbide dissociates into vanadium atomic gas and graphite. The author performed two different indirect methods, one is to analyze the deposit that was formed by condensation of effused gas on the upper part of the furnace tube, and the other is to detect the total weight of effused gas and the residual vanadium in the cell. Both spectroscopic and chemical analyses revealed the deposit is consisted of pure vanadium and no trace of carbon. To do the second proof, 155.3 mg of vanadium carbide, that was accurately weighed, was placed in a degassed graphite cell with an orifice area of 0.021 cm<sup>2</sup>, and it was maintained at 2398°K in high vacuum for 16 hours. The total weight loss minus the weight loss due to the evaporation of graphite cell wall was 59.2 mg. Chemical analysis for the cell gave 66.1 mg as

Table 1 Experimental results for cells without orifice and containing VC.

RUN No.	Temp., °K	Time, hr	Wt. Loss, mg/hr
V 126	2429	7.00	1.41
V 127	2461	10.00	2.45
V 128	2497	10.00	3.51
V 129	2408	10.00	0.96
V 130	2534	7.00	3.40
V 131	2377	10.00	0.24

Table 2 Experimental results for cells with orifice and containing VC and dissociation pressure of VC which is in equilibrium with graphite.

Run No.	Temp., °K	Time, sec.	Wt. Loss, mg	Effective Wt. Loss, mg	P(atm) × 10 <sup>5</sup>
Orifice area a, × 100 = 0.71 cm <sup>2</sup> , k = 0.75					
V 108	2482	16200	23.4	9.81	1.788
V 109	2534	10800	26.1	11.53	3.187
V 110	2377	18000	4.3	3.10	0.498
V 111	2492	19800	31.9	13.20	1.974
V 112	2398	21600	8.1	4.26	0.573
V 113	2419	16200	10.1	5.06	0.911
V 114	2440	21600	21.7	11.50	1.560
V 115	2461	18700	24.3	11.56	1.819
V 116	2398	14400	5.8	3.24	0.654
V 117	2503	18000	29.4	10.75	1.773
V 118	2524	14400	30.6	12.64	2.616
V 119	2545	9000	21.8	8.80	2.927
V 120	2408	19800	9.9	4.62	0.679
V 121	2513	14400	27.3	10.82	2.235
V 122	2346	28800	5.2	3.60	0.359
V 132	2429	32400	25.3	12.61	1.138
V 133	2450	28800	29.7	13.70	1.297

Orifice area a, × 100 = 1.47 cm<sup>2</sup>, k = 0.75

V 123	2513	14400	38.0	21.52	2.147
V 124	2429	28800	33.3	22.02	1.080

Orifice area a, × 100 = 2.12 cm<sup>2</sup>, k = 0.75

V 141	2513	28800	93.60	60.65	2.098
V 140	2429	28800	42.10	30.81	1.048

metallic vanadium, this is, according to the calculation under the foregoing assumption, supposed to be 66.5 mg. The same results are yielded by a number of repeated experiments.

The summary of results are listed in Table 1 and

2. Table 1 shows the weight loss from the cell without an orifice, but containing VC. Subtraction of the weight loss for a run in Table 2 by the corresponding one that is obtained from the smooth curve of Table 1 gives the effective weight loss, which is due to net effusion from the orifice.

In order to check the effect of the orifice area on the observed vapor pressure three different orifice areas have been chosen. If vanadium in the cell is in equilibrium with VC, the amount of vanadium vapor effusing out must be proportional to the orifice area. The effect of the orifice area is discussed in detail by Whitman<sup>(5)</sup> and Motzfeldt.<sup>(6)</sup> The following equation has been derived by Motzfeldt.

$$1/P_{\text{obs.}} = 1/P_{\text{eq.}} + ka/\alpha AP_{\text{eq.}} \quad (4)$$

where  $P_{\text{obs.}}$  and  $P_{\text{eq.}}$  are the observed and equilibrium pressures respectively;  $k$  and  $a$ , the same quantities as before;  $\alpha$  is the accommodation coefficient; and  $A$ , the surface area of vanadium carbide powder.

If  $1/P_{\text{obs.}}$  is plotted as a function of  $ka$  as shown in Fig. 3, equilibrium pressure  $P_{\text{eq.}}$  is obtained from

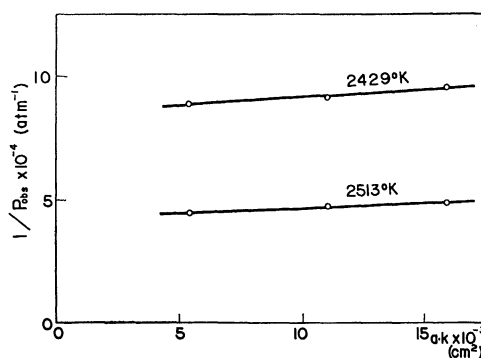


Fig. 3  $a \cdot k$  vs.  $1/P_{\text{obs.}}$

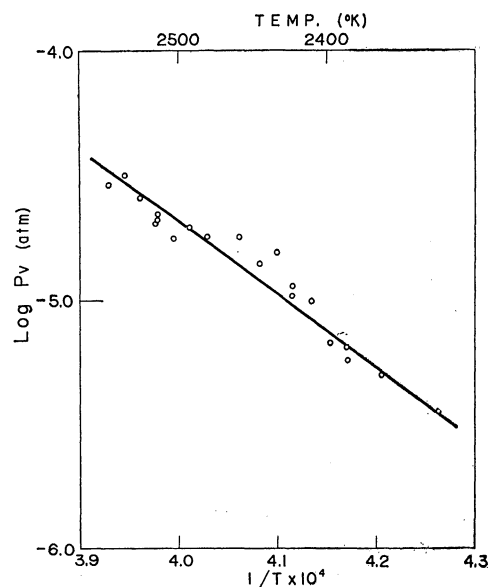


Fig. 4 Dissociation pressure of VC vs. Temperature in the reaction  $\text{VC}(s) = \text{V}(g) + \text{C}(s)$ .

extrapolation of  $1/P_{\text{obs.}}$  to  $ka=0$  and the effective surface area of the sample that supplies vapor, from

(5) C. I. Whitman: J. Chem. Phys., 20 (1952), 161.

(6) K. Motzfeldt; J. Phys. Chem., 59 (1955), 139.

the slope.

From the linear relationship in Fig. 3, it is known Motzfeldt's requirements for equilibrium is satisfied.  $P_{eq.}$  is very close to  $P_{obs.}$ , the difference is much less than the error limitation of this experiment, so then, the observed values can be employed without correction in processing data.

In Fig. 4  $\log P_V(\text{atm})$  versus  $1/T$  is plotted and the most probable line obtained by a statistical method is expressed by

$$\log P_V(\text{atm}) = -30,400/T + 7.50 \quad (5)$$

where  $P_V$  is the dissociation pressure of  $V(g)$  in atmospheres. The corresponding standard free energy change is

$$\Delta F^\circ = 139,100 - 34.32 T \quad (6)$$

Combining the thermodynamic function for each species in Eq. 1 and the standard free energy change determined experimentally at arbitrarily chosen different temperatures, the heat of dissociation at absolute zero,  $\Delta H_{0, \text{diss.}}^\circ$ , was calculated. The results are summarized in Table 3, where the thermodynamic

average value of  $\Delta H_{0, \text{diss.}}^\circ$  is determined to be  $144,636 \pm 2,000$  cal/mol. Combination of this value and the related thermodynamic properties<sup>(9)</sup> yields the heat of dissociation, the standard free energy and entropy change of the reaction at various temperatures, that are tabulated in Table 4.

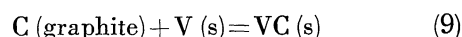
For the vaporization of pure solid vanadium



the standard free energy change<sup>(10)</sup> is given by

$$\Delta F^\circ = 115,800 - 32.32 T \quad (8)$$

Combination of reaction (1) and (7) and their standard free energy change expressed by Eqs. (6) and (8) yields



$$\Delta F_f^\circ = -23,300 + 2.0 T \quad (10)$$

Eq. (10) represents the standard free energy change of formation of VC from supercooled solid vanadium and graphite, and shows that

$$\Delta H_f^\circ = -23,300 \text{ cal/mol}$$

$$\Delta S_f^\circ = -2.0 \text{ e. u.}$$

Table 3 Heat of dissociation of VC at 0°K

Run No.	Temp. °K	$-(F^\circ - H_0^\circ)/T$ V(g)	$-(F^\circ - H_0^\circ)/T$ C(s)	$-(F^\circ - H_0^\circ)/T$ VC(s)	$-\Delta(F^\circ - H_0^\circ)/T$	$\Delta F^\circ$ (exp)	$\Delta H_0^\circ$ diss.
V108	2482	50.13	6.37	19.96	36.54	53,926	144,618
V109	2534	50.25	6.46	20.22	36.51	52,134	144,650
V110	2377	49.87	6.17	19.43	36.61	57,671	144,693
V111	2492	50.15	6.38	20.01	36.52	53,642	144,650
V112	2398	49.92	6.21	19.54	36.59	57,522	145,265
V113	2419	49.98	6.25	19.65	36.58	55,790	144,277
V114	2440	50.03	6.29	19.75	36.57	53,672	142,903
V115	2461	50.08	6.33	19.85	36.56	53,380	143,354
V116	2398	49.92	6.21	19.54	36.59	56,885	144,628
V117	2505	50.18	6.41	20.07	36.52	54,428	145,911
V118	2524	50.23	6.45	20.17	36.52	52,933	145,110
V119	2545	50.28	6.49	20.28	36.49	52,803	145,670
V120	2408	49.95	6.23	19.59	36.59	56,946	145,055
V121	2513	50.20	6.42	20.11	36.51	53,484	145,234
V122	2346	49.79	6.11	19.27	36.63	58,454	144,387
V132	2429	50.00	6.27	19.70	36.57	54,953	143,782
V133	2450	50.05	6.31	19.80	36.56	54,420	143,992
V123	2513	50.20	6.42	20.11	36.51	53,680	145,430
V124	2429	50.00	6.27	19.70	36.57	55,198	144,027
V140	2429	50.00	6.27	19.70	36.57	55,353	144,182
V141	2513	50.20	6.42	20.11	36.51	53,795	145,545

mean  $\Delta H_0^\circ$ , diss. = 144,636 cal/mol

function for VC(s) are newly calculated by the author from the heat capacity data of King<sup>(7)</sup> and Kelley et al<sup>(8)</sup> by integrating it on Gibbs-Helmholtz's equation, and for V(g) and C(s), from the tabulation by Stull and Sinke.<sup>(9)</sup>

In computing values of  $\Delta H_{0, \text{diss.}}^\circ$ , the following equation was employed.

$$R \ln P_V = \frac{(F^\circ - H_0^\circ)/T - (F^\circ - H^\circ)/T}{VC(s) \quad V(g)} - \frac{(F^\circ - H_0^\circ)/T - \Delta H_{0, \text{diss.}}^\circ/T}{C(s)}$$

As shown in column 8 of Table 3, the resulting

Table 4 Thermodynamic quantities for the dissociation of vanadium carbide.

Temp., °K	0	298	2300	2400	2500
$\Delta H^\circ$	144,636	145,573	141,400	140,900	140,400
$\Delta F^\circ$	144,636	134,197	60,295	56,800	53,300
$\Delta S^\circ$	0	38.16	35.3	35.0	34.6

The foregoing equations are applicable to high temperatures above 2000°K. The standard heat of formation of VC at 298°K extrapolated by using available thermodynamic data, is

$$\Delta H_{f, 298}^\circ = -22.8 \text{ kcal/mol}$$

(7) E. G. King: J. Am. Chem. Soc., 71 (1949), 316.

(8) C. H. Shomate and K. K. Kelley: J. Am. Chem. Soc., 71 (1949), 314.

(9) D. R. Stull and G. C. Sinke: *Thermodynamic Properties of the Elements*, Am. Chem. Soc., Washington D.C. (1956).

(10) J. W. Edwards, H. L. Johnston and P. E. Blackburn: J. Am. Chem. Soc., 73 (1951), 4727.

#### 4. Comparison With Other Data

No direct determination of the heat of formation for VC from the elements has been performed up to date.

estimated those thermodynamic quantities, which are not consistent. In Table 5 the standard free energy change and the heat of formation are summarized.

Richardson's estimate is not accurate enough

Table 5 Comparison of thermodynamic properties of VC from various data source.

	$\Delta H_{f,298}^{\circ}$ cal/mol	$\Delta F_{f,298}^{\circ}$ cal/mol	$\Delta S_{f,298}^{\circ}$ e.u.	$\Delta H_{f,2000}^{\circ}$ cal/mol	$\Delta F_{f,2000}^{\circ}$ cal/mol	$\Delta S_{f,2000}^{\circ}$ e.u.
Richardson	-12.5	-12.0	-1.6	-12.5	-9.3	-1.6
Krisorian	-15 ± 8	-14.5 ± 8	-1.6	—	-17.0	—
Elliott and Gleiser	-20 ± 10	-20 ± 10	—	-20.0	—	-1.5
Present work	-22.8	-22.4	-1.6	-23.3	-19.3	-2.0

Richardson<sup>(11)</sup> proposed

$$\Delta F_{f, 293-2000}^{\circ} = -12,500 + 1.6 T$$

which is based on the results by Slade and Higson.<sup>(1)</sup> This yields  $\Delta F_{f, 293}^{\circ} = -12$  kcal and  $\Delta H_{f, 298}^{\circ} = -12.5$  kcal, which are far from the results of the present work. Krikorian<sup>(12)</sup> and Elliott and his coworker<sup>(13)</sup>

to discuss the present problem because of the prescribed reason in the beginning of this report. Present results are in fairly good agreement with Elliott and Gleiser's estimate, that is performed under an assumption the properties of VC is on the extrapolation of NbC and TaC.

#### 5. Acknowledgements

The author wishes to express his deep appreciation to Dr. Gokcen, University of Pennsylvania, for valuable suggestions and discussions in performing this investigation.

(11) F. D. Richardson: J. Iron and Steel Inst., 175 (1953), 33.

(12) O. H. Krikorian: Univ. of California Radiation Lab., No. 2888.

(13) J. F. Elliott and M. Gleiser: *Thermochemistry for Steel-making*, Vol. 1 Addison Wesley Publishing Co. Reading Mass., (1960).