Thermodynamics of order–disorder transformations in vanadium carbide

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Some of the nonstoichiometric carbides of the transition metals (e.g. VC_x) undergo transformations to ordered phases at specific values of x. In a thermodynamic study of such order–disorder transformations the latent heats of the reactions $VC_{0.833} = V_6C_5$ and $VC_{0.875} = V_8C_7$ were measured using differential thermal analysis (DTA) and gave values of $5.7 \pm 2.8 \, \mathrm{cal \, g^{-1}}$ and $6.0 \pm 2.4 \, \mathrm{cal \, g^{-1}}$ (1 cal = 4.1855 J), respectively. For well-annealed specimens intermediate in carbon-to-metal ratio between these two compositions, DTA indicated the coexistence of domains of both ordered phases. The implication is that the nonstoichiometric, disordered, NaCl-structure phase VC_x does not represent the lowest energy state of vanadium carbide at room temperature for any value of x. This result may apply to the other isomorphic carbides, i.e. TiC_x, ZrC_x, HfC_x, NbC_x and TaC_x. The measured temperatures corresponding to the onset of the transformations were $1184 \pm 12°$ C for V_6C_5 and $1112 \pm 8°$ C for V_8C_7, but the centre of the distribution was approximately $50°$ C higher in each case. A rationalization of the existence of first-order transitions and an estimate of the latent heats expected from the measured transition temperatures were attempted using the Bragg–Williams theory of order–disorder transformations. The results are consistent with experiment, though the adequacy of this approximation for such a complex case is questionable.

1. Introduction

A phase transition which produces long-range order in a disordered solid presents a number of interesting implications for experimental and theoretical investigation. For example, the transport properties will be strongly affected, and the thermodynamics of the order–disorder transformation itself can be studied.

Here, we address a complex case, the vanadium–carbon system, in which complete *disorder* is expressed not by intersite exchange of different atoms but by the non-periodic placement of atoms of one kind on lattice sites, many of which are vacant, and *order* is established at specific compositions by diffusion jumps which allow the vacancies to become periodically arranged. We

have previously studied the influence of ordering on electron transport [1, 2], and now we report on the thermodynamics of the order–disorder transformations in vanadium carbide.

2. Order and disorder in transition metal carbides

Vanadium and the other group IVb and Vb transition metals (Ti, Zr, Hf, Nb and Ta) react with carbon to form NaCl-structure (B1) compounds which are severely nonstoichiometric [4–6]. Deviation from stoichiometry is accommodated by vacancies in the fcc carbon sublattice and symbolized by the chemical formula, MeC_x, where Me is one of the above transition metals (in the present case, vanadium) and x is

the carbon-to-metal ratio [4–6]. The atomic fraction of carbon vacancies is thus given by $(1 - x)$.

The vacancies are to a zeroth approximation randomly distributed on the carbon sublattice [6], though short-range order has been detected [7–10]. Compounds belonging to the vanadium–carbon system in the range $0.66 \leqslant x \leqslant 0.88$ can exhibit various degrees of ordering of carbon atoms. Froidevaux and Rossier first detected such ordering by observing the splitting of NMR lines caused by the coupling of the quadrupole moment of ^{51}V atoms to the electric field gradient produced by 0, 1, 2, or 3 vacant nearest-neighbour carbon sites [11]. They observed that the types and intensities of lines present in $VC_{0.875}$ were consistent with an ordered structure. They then investigated lines in the X-ray powder patterns and observed a number of lines in excess of the expected NaCl lines. These observations led them to propose a crystal structure for the first ordered compound, V_8C_7, to be observed in the V–C system in the above range [11].

Venables *et al.* [12] reported a second ordered compound in the range $0.66 \leqslant x \leqslant 0.88$, namely, V_6C_5. They used NMR to identify the types of vacancies on the carbon sublattice and electron diffraction to observe the symmetry of the superlattice caused by ordering of the carbon atoms. They checked the validity of certain spots and the *d*-spacings determined from electron diffraction using X-ray diffraction and a powder specimen.

The ordered compound V_6C_5 can be disordered by electron irradiation, as shown by Venables and Lye [13]. They observed that the electron diffraction spots associated with the superlattice disappear when irradiated by an electron microscope beam with an energy between 33 and 100 keV and estimated that the energy transferred to carbon atoms is approximately $5 \, eV \, atom^{-1}$. Hollox and Venables [14] observed that disordering of V_6C_5 could also be accomplished by thermal fluctuations at temperatures between 1200 and 1300° C.

The influence of the order–disorder transformations $VC_{0.833} = V_6C_5$ and $VC_{0.875} = V_8C_7$ on electron transport was studied by Shacklette and Williams [1, 2] who found evidence that the transitions are first-order: a discontinuity appeared in the electrical resistivity at the critical temperature for ordering, T_c. They also found that the large residual resistivity at low temperatures which

characterized transition metal carbides virtually disappears in the ordered phase as expected when lattice vacancies become part of the periodic potential of the solid.

The existence of ordered phases in transition metal carbides has other implications. One of the concerns that motivated the present study was whether a combination of domains of different ordered phases or a disordered, nonstoichiometric NaCl-structure phase represents the equilibrium state of a carbon-deficient transition metal carbide. In the course of trying to answer that question we have characterized and modelled the thermodynamics of the order–disorder transformations in vanadium carbide and generated experimental and estimated values for the latent heats. For the measurements, differential thermal analysis (DTA) was employed [15], and for the theoretical estimates, the Bragg–Williams (B–W) mean-field theory ([16]; see also abbreviated treatment in Kittel [17]) was adapted to these particular order–disorder transformations, though with many reservations as to its appropriateness.

3. Preparation of powdered samples

The DTA experiments were performed on powdered samples of VC_x, where $0.833 \leqslant x \leqslant 0.875$. The powders were prepared by reacting spectroscopically pure carbon powder and 99.9% pure, 325 mesh, vanadium powder. The desired value of x in the chemical formula VC_x determined the ratios of the constituents. Typically a few grams of thoroughly mixed powders were reacted in a carbon crucible in a Brew vacuum furnace. The furnace temperature was gradually raised to slightly above the temperature at which the powders first began to react, and then it was held constant at about 1400° C until the reaction ceased. Next, the furnace temperature was increased to 2000° C and held for 1 h to allow carbon atoms to distribute themselves throughout the powder by diffusion. Finally, the powders were annealed at 1100° C, just below the O–D transformation temperature, to allow ordered phases to form. The sintered mass that was produced by this procedure was crushed and ground in a boron carbide crucible. The resulting powder was used in the DTA analysis.

4. Differential thermal analysis (DTA)

The latent heat associated with formation of the ordered phases in vanadium carbide was investi-

gated by standard differential thermal analysis (DTA), though an attempt was also made to use an a.c. calorimetric technique in which an a.c. current heats a single crystal specimen and its periodic temperature variation is sensed with a lock-in amplifier. However, because of the slow kinetics of the vanadium carbide phase transformations (several seconds according to electrical resistivity studies by Shacklette and Williams [1]) the a.c. technique was not feasible. This large time-constant is determined by slow diffusion, with an activation energy for carbon migration of $4-5\,eV\,atom^{-1}$, which, in turn, reflects the strong bonding in this solid [18, 19].

The data for a DTA experiment are plotted by an $x-y$ recorder with the reference thermocouple voltage, V_R, plotted on the x-axis and the differential thermocouple voltage, ΔV, plotted on the y-axis. The area, A, between the background curve and the peak drawn a first-order phase transition is related to the latent heat, λ, of the transition being investigated. The equation relating λ and A is:

$$\lambda = \frac{KA}{m_s R}, \qquad (1)$$

where m_s is the mass of the sample, R is the heating rate of the sample, K a constant and A the area. Fig. 1 shows the apparatus.

The DTA apparatus (Dupont Model 900) was calibrated with materials having first-order transitions of known latent heats: (1) gold (fusion
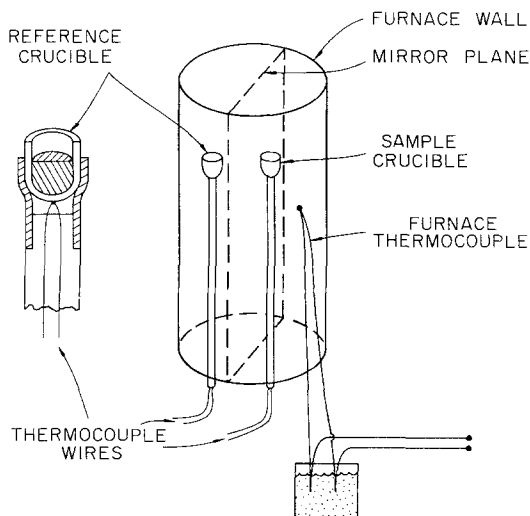

Figure 1 The location of sample and reference powders within the DTA furnace. The furnace thermocouple is used by the furnace control unit.

at $1063°\,C$); (2) nickel (fusion at $1453°\,C$); and (3) iron (crystal structure change at $907°\,C$). These materials were placed in alumina crucibles and heated at rates comparable to that for V_6C_5. Then for each material the area of three runs was determined by repeated planimetering. For the set of areas from one sample, the root mean square (rms) deviation from the average was typically about 1%. The slope of the least-squares line was $0.947\,min\,°C\,cal^{-1}$ (Table I and Figs. 2 and 3), and the resulting value of the latent heat of the transition $VC_{0.833} = V_6C_5$ was $5.68\,cal\,g^{-1}$ (Fig. 4). The transition is thus confirmed to be first-order.

For a comparison between V_6C_5 and V_8C_7, and for the rest of the work described here, sample and reference were placed in identical crucibles of platinum instead of the alumina ones used to obtain data for the calibration line. The platinum crucibles could not be used to construct the calibration line, because platinum and gold combine at high temperatures, but are preferable because platinum is a better thermal conductor.

The areas of the V_8C_7 and V_6C_5 transitions from experiments that used the platinum crucibles were planimetered and compared by forming the ratio

$$\gamma = \frac{8}{6} = \frac{m_{s6}}{m_{s8}}\,\frac{R_6}{R_8}\,\frac{A_6}{A_6}, \qquad (2)$$

where all quantities have been previously defined. (V_6C_5 is designated by a subscript 6, etc.) The value of γ obtained from the data was $\gamma = 1.06$.

The latent heat of the V_8C_7 transition can be calculated from Equation 2 and the latent heat of V_6C_5 that was determined by DTA. The result is $\lambda_8 = 6.02\,cal\,g^{-1}$. Consideration of the calibration uncertainty and other instrumental errors leads to a total uncertainty of $\pm 40\%$ for the DTA values of λ.

5. Measurements of transition temperature, T_c

The first detectable separation of background and experimental curves yields two coordinates on the graph paper: T_R $(= x)$, and $\Delta T = T_S - T_R$ $(= y)$. Here ΔT represents the slight background difference in temperature between the reference and sample. From these, the critical temperature for the order—disorder transformation is calculated:

$$T_c = T_{Rc} + \Delta T_c, \qquad (3)$$

TABLE I Latent heat calibration table

Transition	Mass (g)	Rate (mV min⁻¹)	Area (10³ mV²)	x (min °C g⁻¹)	Lat. heat (cal g⁻¹)
Fe	0.114 19	0.62	1.28	1.38	3.91 [26]
			1.61	1.74	
			1.24	1.34	
Au	0.148 60	0.53	19.5	18.5	15.3 [26]
			19.7	18.7	
			19.4	18.4	
Ni	0.045 41	0.56	23.0	65.2	71.7 [26]
			23.9	67.7	
			24.2	68.6	
(V$_6$C$_5$	0.070 22	0.57	3.07	5.56	0.68†)
			2.82	5.11	
			2.88	5.22	

†From calibration curve established by above standards — for comparison.

where subscript c denotes a value at the sample's T_c.

For this work the correction term ΔT_c was determined by starting the experiment when sample, reference, and furnace were in thermal equilibrium. A DTA graph was made as the sample was heated at a constant rate R $(= dT/dt)$. The ΔT_cs obtained from a set of such graphs produced by various heating rates show that $\Delta T_c = -7.2 \pm$ 0.5° C over a range of R of a factor of two (Table II). This value of ΔT_c and the observed values of T_{Rc} were used to calculate values of T_c from Equation 3 (Table III): $1184 \pm 8°$ C for T_{C6} and $1110 \pm 3°$ C for T_{C8}. These uncertainties reflect only precision of measurement — for an estimate of absolute accuracy we add 5° to these uncertainties, making $\pm 13°$ C and $\pm 8°$ C, respectively.
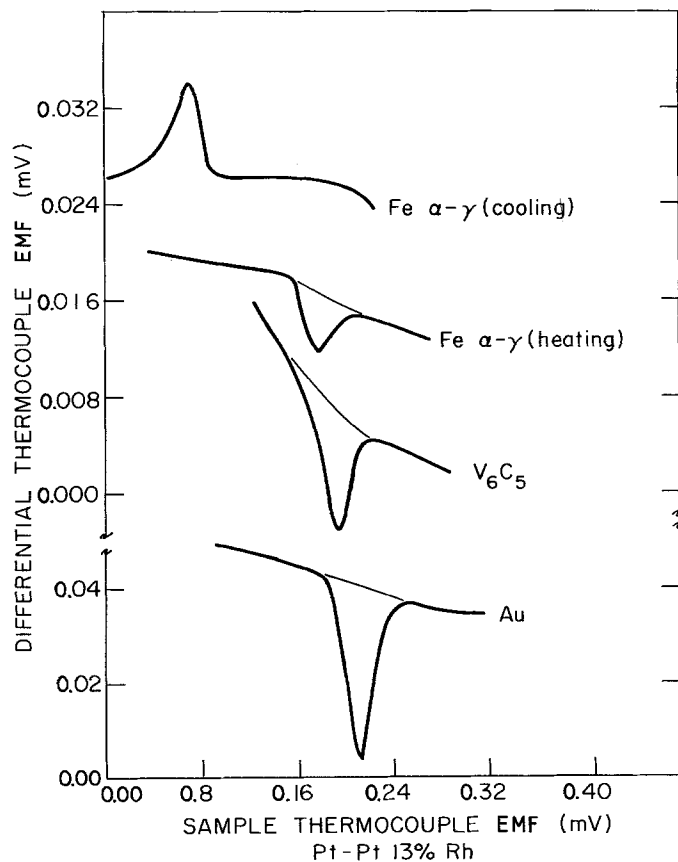
The values of T_c given above and listed in Table

Figure 2 DTA curves for calibration samples.

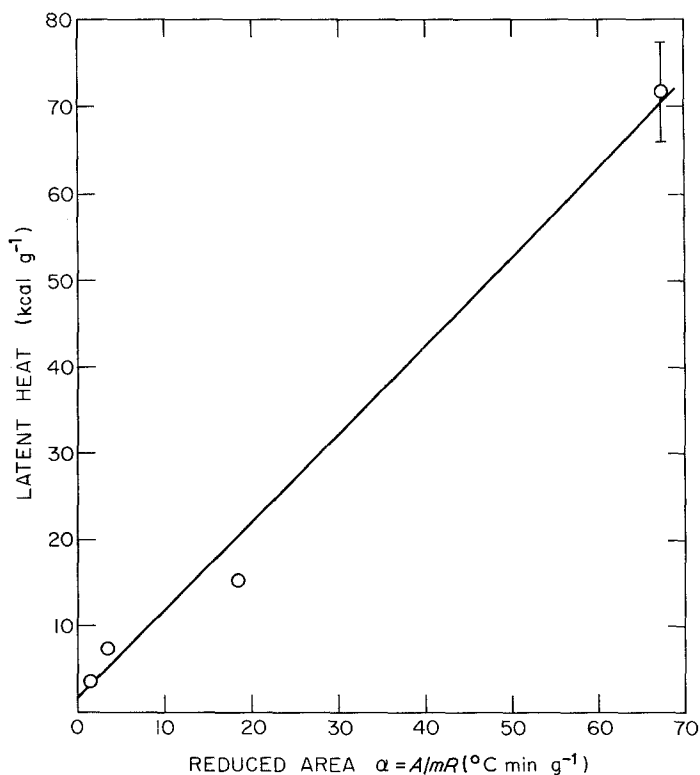V were taken from the first deviation of the DTA differential thermocouple voltage from the background curve. The rapid increase in the signal (determined from the inflection point in the integrated curve) always took place at values of T approximately $50°$ C higher.

6. DTA study of presence of both transitions in VC_x powders

The DTA experiments gave evidence of the existence of both a V_6C_5 and a V_8C_7 transition in VC_x powders having carbon concentrations higher than that of V_6C_5 but less than that of V_8C_7 ($0.833 \leqslant x \leqslant 0.875$). Some of the T_c data in Table V, for example, are from VC_x powders in this range. Also, powders initially of composition V_8C_7 developed two transitions as time went on.

DTA experiments were performed repeatedly: (1) on a V_8C_7 sample, (2) on a few VC_x powders with different values of x, and (3) on V_6C_5 samples. The results of the repeated DTA experiments on a V_8C_7 sample are typical of those for the VC_x samples. The graphs obtained from repeated cycling of a V_8C_7 sample (Fig. 5) have both a V_8C_7 and a V_6C_5 dip. The area of the V_8C_7 dip decreases (Fig. 6) as time evolves, and the area of the V_6C_5

dip increases. The ratio M of the V_6C_5 area to the total area can be used to compare the relative size of the areas:

$$M = \frac{A_6}{A_6 + A_8} \qquad (4)$$

where A_I is the area of a dip, and $I = 8$ for V_8C_7, 6 for V_6C_5.

After each experiment, the temperature of the furnace was lowered to about $1100°$ C and held there for about 0.5 h to let the sample reorder. This annealing time was recorded. The ratio M was plotted against elapsed annealing time and found to increase as annealing time increased (Fig. 6).

The magnitude of M for VC_x powders was also investigated. A series of powders having carbon-to-metal ratios intermediate between those of V_8C_7 and V_6C_5, i.e. with $x = 0.843, 0.853$, and 0.864, was produced. Results showed that M for $VC_{0.864}$ is smaller than M for $VC_{0.883}$.

Fig. 7 shows typical graphs for each powder. The graphs have two dips, one each at the V_6C_5 and V_8C_7 critical temperatures. The dips occurred at the same temperatures throughout a series of experiments (Table V), but the areas, and hence the ratio M, changed in a systematic way with
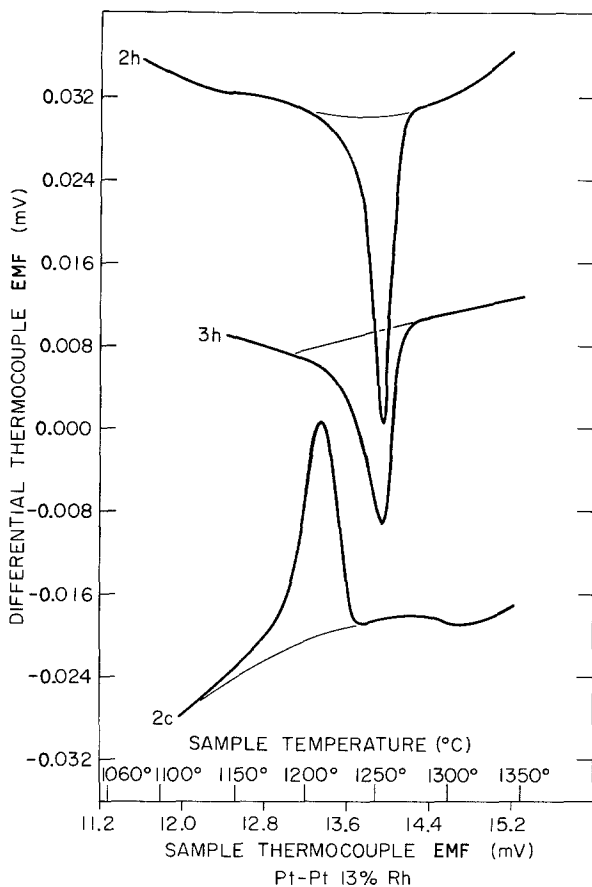
Figure 4 Typical heating (2h) and cooling (2c) curves for DTA experiments on V_6C_5.

number of cycles, probably due to vaporization and/or oxidation of the samples.

A simple explanation of why M is different for different values of x is that the powders are a mixture of small domains of both compounds. The initial value of M for a powder can be predicted by assuming that all carbon atoms that were originally reacted to form VC_x are incorporated into either the V_6C_5 or the V_8C_7 domains. If this is true, a specimen containing N_T vanadium atoms and xN_T carbon atoms (where $0.833 \leqslant x \leqslant 0.875$) would segregate into N_6 units with composition V_6C_5 and N_8 units with composition V_8C_7. Since no vanadium or carbon atoms are lost, N_6 and N_8 would satisfy

$$N_T = 6N_6 + 8N_8 \qquad (5)$$

and

$$xN_T = 5N_6 + 7N_8. \qquad (6)$$

These specify N_6 and N_8 for all x.

The amount of heat associated with each transition is $N_8 m_8 \lambda_8$ for V_8C_7, and $N_6 m_6 \lambda_6$ for V_6C_5 (where m_8 is the mass of a unit of V_8C_7, etc.) Thus the ratio M is

$$M = \frac{N_6}{N_6 + (N_8 \lambda_8 m_8 / \lambda_6 m_6)}. \qquad (7)$$

But $\lambda_8 = 1.06 \lambda_6$ by DTA work. Thus

$$M = \frac{N_6}{N_6 + 1.425 N_8} \qquad (8)$$

TABLE II Temperature differences $T (= T_S - T_R)$ at T_t

	R ($^\circ K \, min^{-1}$)	T_I ($^\circ C$)
	21	−6.66
	28	−7.52
	35	−6.16
	42	−8.45
Average		−7.2 ± 0.5

TABLE III V_6C_5 and V_8C_7 critical temperatures

Sample	T_{c6} ($^\circ C$)	N_6	T_{c8} ($^\circ C$)	N_8
V_6C_5	1188 ± 9.5	16		
V_8C_7	1188 ± 12.1	6	1099 ± 5.5	8
$VC_{0.843}$	1187 ± 15.6	3	1107 ± 4.5	3
$VC_{0.853}$	1187 ± 25.3	2	1110 ± 9.1	2
$VC_{0.864}$	1168 ± 17.8	3	1111 ± 2.8	4
Average	1184 ± 8		1110 ± 3	

TABLE IV Numbers of bonds and interaction energies		
C–C	$Q_{AA} = NzF_A^2 (1-S^2)/2$	$-v_{AA}$
Vac–Vac	$Q_{BB} = Nz (F_B^2 - S^2 F_A)/2$	$-v_{BB}$
C–Vac	$Q_{AB} = NzF_A (F_B + F_A S^2)$	$-v_{AB}$

where

$$N_6 = \frac{N_T}{2}(7 - 8x) \qquad (9)$$

and

$$N_8 = \frac{N_T}{2} (6x - 5). \qquad (10)$$

The line

$$M = 3(7 - 8x) \qquad (11)$$

is a good approximation to the exact curve of the plot of M against X obtained from Equations 8 to 10.

7. Application of the Bragg–Williams theory

A unit cell of a V_6C_5 crystal contains 99 atoms, 54 vanadium and 45 carbon, and in addition has 9 ordered vacancies on the carbon sublattice [11].

TABLE V Results of the B–W theory				
Formula	S_t	v/kT_t	λ/NkT_t^*	λ (cal g^{-1})†
V_6C_5	0.6340	1.1690	0.1566	7.421
V_8C_7	0.7143	1.7944	0.1717	7.580

$^*zS^2 F_B^2(N/kTt)$

Nine "molecules" of V_6C_5 comprise the unit cell, and each has its centre on a vacancy site. The order–disorder transition occurs on the carbon sublattice at high temperatures as carbon atoms and vacancies randomly exchange places while the vanadium atoms undergo only slightly adjustments in spacing. However, the symmetry of the structure changes from trigonal to cubic in $V_6C_5 \rightarrow VC_{0.833}$.

In view of the complexity of this crystal structure, the Bragg–Williams (B–W) description of the order–disorder transformation [16, 17] was selected because it requires a minimum of detailed counting of bonds. Although it is an approximate, mean-field theory, it appears to be the only approach that makes the problem tractable. Whether the results obtained are
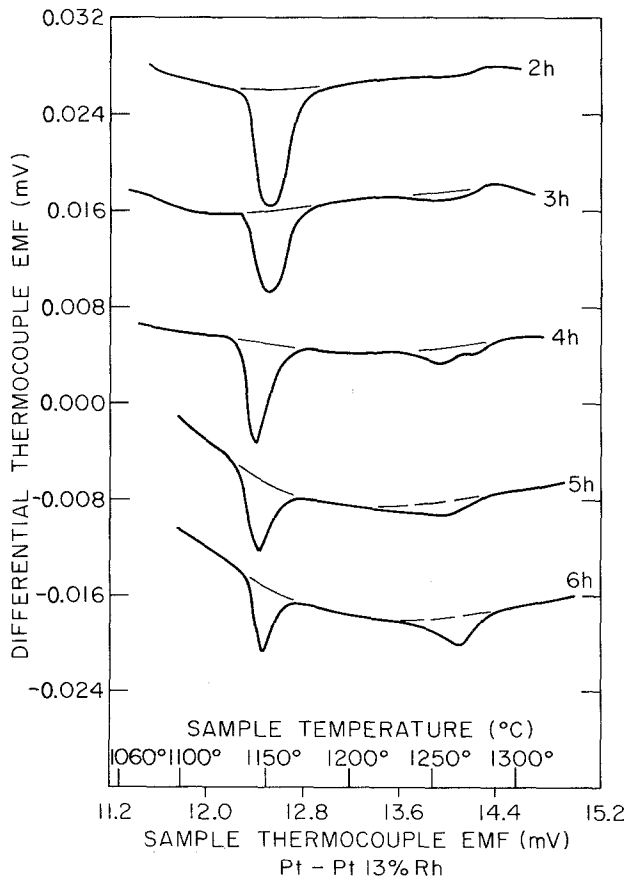

Figure 5 A sequence of DTA experiments on V_8C_7 which show the growth of the V_6C_5 transition as time increases.
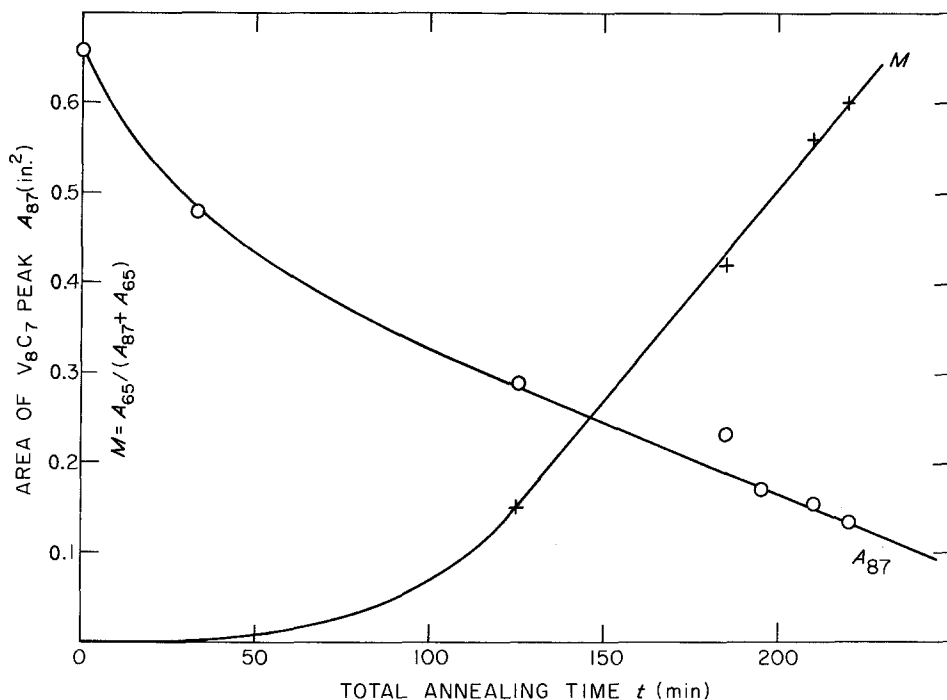
Figure 6 Increase of the area ratio M as annealing time increases. The decrease of the area of the V_8C_7 transition is also shown. 1 in.^{2} = 6.4516 × 10^2 mm^2.

meaningful is open to question, but we include the analysis as it does generate results consistent with the experiment.

We assume:

(1) next-neighbour interactions between carbon atoms and vacancies, which are nearest-neighbours on the carbon sublattice;

(2) a constant interaction energy between vanadium and carbon atoms irrespective of the degree of ordering of the carbon sublattice (and a similar assumption for the interaction involving vacancies);

(3) the usual assumption due to Bragg and Williams (the number of bonds of a given type for a given degree of order is equal to the statistical average of the number of bonds, which is hereafter designated by brackets).

The B–W theory is adapted to V_6C_5 by treating only the carbon sublattice, since, to a first approximation, the vanadium atoms are not involved in the $VC_{0.833} = V_6C_5$ transition. The positions of carbon (A atoms) and carbon vacancies (B atoms) in the perfect crystal then define the α and β sublattices, respectively. The number of bonds, Q_{IJ}, between various atoms and their interaction energies, v_{IJ} (I, J = A, B), can then be listed (Table IV). In terms of the tabulated quan-

tities, the average internal energy, U, of the carbon sublattice is:

$$U = -\langle Q_{AA}\rangle v_{AA} - \langle Q_{BB}\rangle v_{BB} - \langle Q_{AB}\rangle v_{AB}.$$

$$(12)$$

If N_A is the number of A (carbon) atoms on the carbon sublattice, and N is the total number of atoms, then the fraction F_A of all atoms that are type A is given by:

$$F_A = N_A/N. \qquad (13a)$$

A similar fraction F_B describes the number of B atoms, i.e. carbon vacancies:

$$F_B = N_B/N. \qquad (13b)$$

N_A and F_A are, respectively, the number and fraction of the total carbon sublattice sites that are α sites, and N_B and F_B apply to β sites.

If r_α is the fraction of α sites correctly occupied, then the fraction of sites incorrectly occupied is $w_\alpha = 1 - r_\alpha$. We now introduce the B–W order parameter, S, ($0 \leqslant S \leqslant 1$) and write for the fraction of incorrectly-occupied α sites

$$w_\alpha = 1 - r_\alpha = F_B (1 - S). \qquad (14)$$

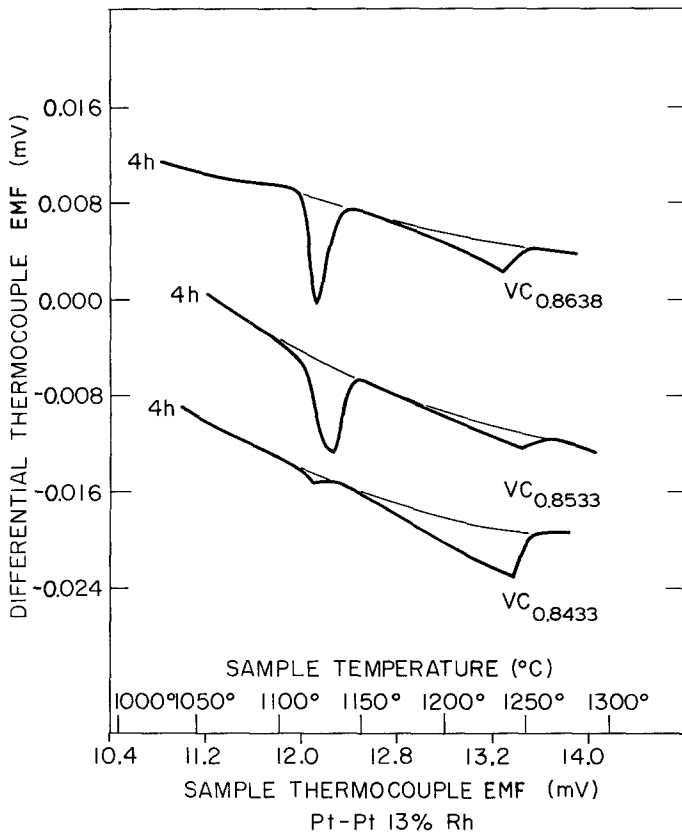Similarly, the fraction of incorrectly occupied β sites is

Figure 7 Typical DTA experiment curves for $VC_{0.843}$, $VC_{0.853}$, $VC_{0.86}$.

$$w_\beta = 1 - r_\beta = F_A(1 - S). \quad (15)$$

The equilibrium value of the order parameter S for a given temperature is the value that minimizes the Helmholtz free energy, F:

$$F = U - TS_c, \quad (16)$$

where the internal energy, U, is given by

$$U = -Nz F_B^2 S^2 v + E_0, \quad (17)$$

with v, the ordering potential, defined by the expression

$$v = v_{AB} - (v_{AA} + v_{BB})/2,$$

and E_0 defined by the expression

$$E_0 = -Nz(F_B^2 v_{BB} + F_A^2 v_{AA} + 2F_A F_B v_{AB})/2. \quad (19)$$

The quantity z is the number of nearest neighbours on the carbon sublattice ($z = 12$).

The configurational entropy of the lattice, S_c, is

$$S_c = k \ln W(\alpha)W(\beta) \quad (20)$$

where

$$W(i) = \frac{N_I!}{(N_I r_i)!(N_I w_i)!} \quad (21)$$

where $i = \alpha, \beta$; $I = A, B$; $\alpha \Leftrightarrow A$, $\beta \Leftrightarrow B$, and $k =$ Boltzmann's constant.

Stirling's approximation for the factorial and some algebraic manipulation can be used to simplify S_c to obtain

$$S_c = Nk \left\{ F_A \left[\ln\left(\frac{1}{r_\alpha}\right) + w_\alpha \ln\left(\frac{r_\alpha}{w_\alpha}\right) \right] \right.$$
$$\left. + F_B \left[\ln\left(\frac{1}{r_\beta}\right) + w_\beta \ln\left(\frac{r_\beta}{w_\beta}\right) \right] \right\}. \quad (22)$$

When Equations 20 to 22 are substituted into Equation 16, the result is an expression for the free energy of the lattice as a function of S and T:

$$F(S) = E_0 - NzF_B^2 vS^2 - kTN \left[F_A \left\{ \ln\left(\frac{1}{r_\alpha}\right) \right. \right.$$
$$\left. + w_\alpha \ln\left(\frac{r_\alpha}{w_\alpha}\right) \right\} + F_B \left\{ \ln\left(\frac{1}{r_\beta}\right) + w_\beta \ln\left(\frac{r_\beta}{w_\beta}\right) \right\} \right],$$
$$\quad (23)$$

where r_i and w_i are given by Equations 3 and 4 and are functions of S. The free energy of the system when $S = 0$ is

$$F(0) = E_0 + kTN \left[F_A \ln F_A + F_B \ln F_B \right]. \tag{24}$$

When the free energy is minimized with respect to S and simplified, the result is an equation that relates S and T:

$$2zvS/kT = (F_A/F_B) \ln \{ [1 + (F_B/F_A + F_A/F_B)S + S^2]/(1 - S)^2 \}. \tag{25}$$

If the free energy for $S \neq 0$ becomes equal to the free energy for $S = 0$, then a first order transition can occur. An equation that has a solution $S \neq 0$ when a first order transition occurs can be obtained by setting $F(S) = F(0)$ and substituting Equation 25 into Equation 23 to obtain

$$F_A (1 - S/2) = \frac{\ln |S_\rho + 1| + \rho \ln |S/\rho + 1|}{\ln [(S^2 + \alpha S + 1)/(1 - S)^2]} \tag{26}$$

where

$$\rho \equiv F_A/F_B$$

and

$$\alpha \equiv \rho + 1/\rho.$$

Solutions for both V_6C_5 ($F_A = 5/6$, $\rho = 5$, $\alpha = 5.20$) and V_8C_7 ($F_A = 7/8$, $\rho = 7, \alpha = 7.143$) were found. Thus the occurrence of the first-order transitions $VC_{0.833} = V_6C_5$ and $VC_{0.875} = V_8C_7$ is consistent with the B–W treatment. The value of S at the transition temperature, T_t, is given in Table V for each case.

The B–W estimate of the latent heat, λ, associated with a first-order phase transition is calculated from the change in internal energy, ΔU, at T_t:

$$\Delta U = NzF_B^2 vS_t^2, \tag{27}$$

where $S = S_t$ when $T = T_t$, and from the ratio r,

$$r = \frac{zv}{kT_t}, \tag{28}$$

which is obtained by substitution of S_t into Equation 25. The result is

$$\lambda = NkT_t (zF_B^2S_t^2r). \tag{29}$$

The latent heat is thus expected to be proportional to the critical temperature of the transition.

The B–W formulation of the entropy change on disordering, S_c, is obtained from Equation 18 by use of the following equation:

$$S_c = \frac{\lambda}{T_t} = (z F_B^2 S_t^2 r) Nk. \tag{30}$$

To evaluate the B–W estimates of λ and S_c for the case of vanadium carbide, the values of T_t obtained from the DTA experiments (see Section 5) were substituted into Equations 29 and 30. The results are included in Table II.

8. B–W description of coexistence of two phases

Since a number of DTA experiments points to the existence of vanadium carbide powders that are mixtures of V_8C_7 and V_6C_5, we examine the B–W formulation of the Gibbs free energy, G, of compounds formed from disordered VC_x to see whether coexistence of these two phases is consistent with B–W.

$$G_x = N_T E_{0X} - TS_{dx} + pV'_x = gxN_T, \tag{31}$$

where: $E_{0x} + pV'_x$ is approximately constant with respect to temperature; E_{0x}, the interaction energy of the random carbon sublattice, is found by substitution of x for F_B and $1 - x$ for F_A in Equation 8, for F_A ($= 0.833$) $\leqslant x \leqslant F_B$ ($= 0.875$); p is pressure; V' is used for volume because V has been used for vanadium; and N_T is the total number of carbon sublattice sites in the powder. S_{dx}, the entropy of the disordered carbon sublattice, is found by substitution of $S = 0$ into Equation 22. (The substitution of x for F_B etc. is used here also.) Thus

$$S_{dx} = -k [x \ln x + (1 - x) \ln (1 - x)] N_T. \tag{32}$$

The slope of a plot of G_x against T is S_{dx}.

If at T_{t6} the disordered powder VC_x develops ordered V_6C_5 and V_8C_7 domains, then the Gibbs free energy of the segregated compound, G_{seg}, must satisfy the inequality

$$G_{seg} = 6N_6g_6 + 8N_8g_8 \leqslant N_Tg_x, \tag{33}$$

where $g_I =$ the free energy of V_6C_5 ($I = 6$), or of V_8C_7 ($I = 7$), or of VC_x ($I = x$) per lattice site, $6N_6 =$ the number of sublattice sites of V_6C_5 and $8N_8 =$ the number of sublattice sites of V_8C_7. Equation 33 can also be written as

$$N_T [g_6 + (x - 5/6) 24 \Delta g] \leqslant N_T g_x, \qquad (34)$$

where

$$\Delta g = g_6 - g_8 = E_{06} - E_{08} - T_{t6} (S_{d6} - S_{d8})$$
$$+ p (V_6' - V_8')/N_T. \qquad (35)$$

One possible situation is that $\Delta g = 0$. This case will be discussed after the more general case. If $\Delta g \neq 0$, then Equation 35 can be simplified by noting that

$$S_{dx} \cong S_{d6} + (x - 5/6) 24 (S_{d8} - S_{d6}) \quad (36)$$

is an excellent approximation. When this is substituted into Equation 35 the result is

$$E_{06} + p \left(\frac{V_6'}{N_T} \right) + (x - 5/6) 24 \left\{ E_{06} - E_{08} \right.$$
$$\left. + p \left[\frac{(V_6' - V_8')}{N_T} \right] \right\} \leqslant E_{0x} + p \left(\frac{V_x'}{N_T} \right). \quad (37)$$

All energies (E_{ds}) and entropies are comparable to kT_{t6} while at atmospheric pressure

$$pV_x' \sim 0.003 \, k \, T_{t6}.$$

Then since

$$\frac{V_x' - V_6'}{N_T} \sim 0.01 \, \frac{V_6'}{N_T} \sim 3 \times 10^{-5} \, kT_{t6},$$

(for $0.833 \leqslant x \leqslant 0.875$) all terms involving differences in volume are negligible compared to other terms and can be dropped. With this simplification, Equation 37 can be written as

$$E_{06} + 24(x - 5/6)(E_{08} - E_{06}) \leqslant E_{0x}. \quad (38)$$

If Equation 19 is written as a function of x, and Equation 18 for v is substituted into the result, the energy of the disordered solid can be rewritten as

$$E_{0x} = z \left[wx^2 - x(v_{AB} - v_{AA}) - \frac{v_{AA}}{2} \right], \quad (39)$$

where v is given by Equation 18. In addition to the x dependence shown explicitly, v also depends on x implicitly. This is evident in the prediction of the B–W calculations (Table II) and is confirmed by experiment:

$$v_6 = 1.1690 \, kT_{t6} \qquad (40)$$

$$v_8 = \left(1.7944 \frac{T_{t8}}{T_{t6}} \right) kT_{t6} = kT_{t6}$$

$$= 1.7944 \, kT_{t8}. \qquad (41)$$

Thus at least one, if not all, of the interaction energies (v_{AB} etc.) in Equation 39 depend on x.

Since the interaction energies (v) are functions of x, it is possible at T_{t6} to have $g_6 = g_8$. Then

$$g_6 \leqslant g_x \qquad (42)$$

(for $0.833 \leqslant x \leqslant 0.875$). The equal sign in Equation 42 applies when $x = 5/6$ or $7/8$. If the pV' products are negligible,

$$E_{0x} \geqslant T_{t6} (S_{dx} - S_{d6}) + E_{06} =$$
$$= 24(x - 5/6) (S_{d8} - S_{d6}) T_{t6} + E_{06}. \quad (43)$$

To obtain the equation at the far right, Equation 36 was used to approximate S_{dx}.

Insofar as the calculated free energies approximate the chemical potentials, if $g_6 = g_8$, then V_6C_5 and V_8C_7 can coexist indefinitely in diffusive contact. The solid is then a two-phase, heterogeneous mixture, according to the results of this approximate theory.

9. Discussion

The presence of such high vacancy concentrations as are found in nonstoichiometric transition metal carbides (up to 50% in the carbon sublattice) without a phase transition to a more stable state has been puzzling for some time. The present study suggests both theoretically and experimentally that this highly disordered system is not, in fact, the lowest energy state at ordinary temperatures.

Not only does vanadium carbide (VC_x) undergo a transition to an ordered compound for two specific values of x, but for intermediate values, the material, if carefully annealed, will develop regions of *both* ordered phases such that the *average* carbon-to-metal ratio equals the value of x in the starting VC_x.

If ordered domains are the lowest energy state, why is vanadium carbide generally found in the disordered nonstoichiometric NaCl structure, VC_x? For the ordered phase to occur, diffusive jumps of carbon atoms into vacant lattice sites are necessary. Now the activation energy for such jumps (e.g. the migration energy for vacancy diffusion) is an extraordinarily large number — approximately 4.5 eV atom^{-1} for transition metal carbides according to the ^{14}C tracer diffusion measurements on single crystals by Sarian [18] and Sarian and Criscione [19]. (Note that for a compound with abundant vacancies already present, formation of vacancies by thermal fluctu-

ations is not required for diffusion so a measurement of the diffusional energy yields the migration energy directly.) With such a high energy barrier for diffusion, the formation of ordered domains can be kinetically limited at moderate temperatures, and unless long and careful annealing just below the transition temperature is carried out, the disordered phase can be quenched in.

Although this description applies specifically to vanadium carbide, the material investigated in this study, the comments are probably applicable to NbC_x and TaC_x. These materials are also formed from group Vb metals, are isomorphic with VC_x, and exhibit ordered phases at specific values of x.

The IVb transition metal carbides TiC_x, ZrC_x and HfC_x are isomorphic with the Vb carbides and share their mechanical, thermal and electrical properties (except for superconductivity). Thus by analogy some tendency towards ordering might be expected in these three materials, although the 5/6 and 7/8 examples discussed here are not exhibited (perhaps again because of sluggish diffusion).

The above discussion suggests (though evidence is advanced for only one of six members of the class) that the NaCl-structure transition metal monocarbides, which are often regarded as severely nonstoichiometric compounds, are actually quenched in this condition and are not in their equilibrium states until the temperature is high enough for disorder entropy to justify this phase. If correct, this conclusion alters a common conception of these refractory compounds in an important way.

In practice, however, the carbides are found in the disordered NaCl-structure phase following materials synthesis and processing, so technical data pertaining to this phase remain useful and appropriate for typical material.

If vacancy ordering is indeed a universal tendency in transition metal carbides, what accounts for the interaction? Toth suggested earlier that Coulomb repulsion of charged vacancies might be responsible [4]. To investigate this idea we note that the ordering potential, v, of Equation 18,

$$v = v_{AB} - \tfrac{1}{2}(v_{AA} + v_{BB}),$$

if written in terms of Coulomb interactions involving charged A atoms (carbon) and charged B atoms (vacancies), takes the following form:

$$v = k\frac{q_A q_B}{r_{AB}} - \frac{1}{2}\left(k\frac{q_A q_A}{r_{AA}} + k\frac{q_B q_B}{r_{BB}}\right)$$

$$= \frac{k}{r}(q_A q_B - \tfrac{1}{2}q_A^2 - \tfrac{1}{2}q_B^2)$$

$$= -\frac{k}{2r}(q_A - q_B)^2, \qquad (44)$$

where r is the next-nearest neighbour separation in the NaCl structure, as only these interactions were considered in the B–W analysis. That is, if the carbon atoms and vacancies interact through the long-range Coulomb potential, then the difference in the interaction which leads to ordering could also be Coulombic and would be representable by the difference in charge between a carbon atom and a vacancy. The form of this result may not be unique to Coulombic interactions but it is consistent with it. Screening by the conduction electron gas should also be included.

Is there any reason to expect carbon atoms and vacancies to be charged at all? Early ESCA experiments on TiC by Ramquist et al. [20] indicated that the observed energy shifts with respect to the element could be explained by charge transfer from the metal atom to the carbon. Although the amount of the transfer originally inferred appeared to be enough to account for the heat of formation of the compound through Coulombic interactions alone, later discussions taking into account many-body effects reduced the amount of the charge transferred but did not alter the sense. The many band-structure calculations which have been done on the transition metal carbides agree that there is some transfer of charge (particularly in the IVb compounds) and the sense of it is from metal to carbon (see, for example, [21–24]). (One early calculation gave the opposite result, but it has been superceded.) Thus we note that there is both theoretical and experimental support for the idea that carbon in the transition metal carbides bears a net charge (though the concept is ambiguous, depending on how the charge is defined.) If so, then the carbon vacancy must also be charged but with a different value.

The sense of the Coulomb interaction of charged vacancies, discussed above, would necessarily be repulsive, as they would have charges of the same sign. Is there any independent evidence for such a repulsive interaction of nearest neighbour vacancies?

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In the case of V_8C_7, the carbon vacancies occupy only third nearest-neighbour sites in the carbon sublattice of the NaCl-structure $VC_{0.875}$ from which the ordered phase develops, according to the neutron scattering results of de Novion and Moisy-Maurice [7], They interpreted the corresponding third nearest-neighbour vacancy—vacancy interaction term as attractive, while terms representing first, second, fourth and fifth nearest-neighbour interactions were taken to be repulsive. Thus the present model of repulsive nearest-neighbour interactions is consistent with one of the results of de Novion and Moisy-Maurice for V_8C_7, though the model includes only the leading term. A similar statement can be made for V_6C_5, though here vacancy pairs also occupy fourth and fifth nearest-neighbour sites.

An analysis of the geometrical opportunities for carbon vacancy ordering in VC_x was made by Kanamori [25]. He considered the possible vacancy pairs, p_1, p_2, p_3, p_4, p_5, referring to nearest-neighbours, second nearest-neighbours, etc., and showed that $x = 0.875$ is the maximum value for which $p_1 = p_2 = p_4 = p_5 = 0$, and that $x = 0.833$ is the maximum value for which $p_1 = p_2 = 0$. These findings are consistent with the neutron scattering data of de Novion and Moisy-Maurice [7].

In the formulation of the statistical analysis (the Bragg—Williams mean field theory) it is assumed that only long-range order or complete disorder can exist. In reality, short-range order above and below the critical temperature is found [7—10]. However, in view of the complexity of this system, it was decided not to attempt to apply any theories which include short-range order.

The B—W analysis was consistent with the occurrence of first-order phase transitions. Values estimated for the latent heats of $V_6C_5 = VC_{0.833}$ and $V_8C_7 = VC_{0.975}$ were of the same order of magnitude as the measured values but higher by approximately the same percentage, 30%. Hence the ratio of the heats was fairly accurately given, though in view of the approximate nature of the treatment, such agreement may be fortuitous.

Acknowledgements

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