

## The Heat of Dissociation of Carbon Monoxide

George Glockler

Citation: [The Journal of Chemical Physics](#) **18**, 1517 (1950); doi: 10.1063/1.1747533

View online: <http://dx.doi.org/10.1063/1.1747533>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/18/11?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Electronimpact dissociation of carbon monoxide](#)

J. Chem. Phys. **98**, 7804 (1993); 10.1063/1.464588

[Metastable Dissociation of the Doubly Charged Carbon Monoxide Ion](#)

J. Chem. Phys. **53**, 132 (1970); 10.1063/1.1673756

[Dissociation Energies of Carbon Monoxide and Nitrogen from Reflected Shock Wave Studies](#)

J. Chem. Phys. **26**, 655 (1957); 10.1063/1.1743363

[Dissociation Energy of Carbon Monoxide](#)

J. Chem. Phys. **24**, 1103 (1956); 10.1063/1.1742688

[Gaseous Detonations. III. Dissociation Energies of Nitrogen and Carbon Monoxide](#)

J. Chem. Phys. **20**, 876 (1952); 10.1063/1.1700587

---



## The Propagation of Order in the Simple Cubic Lattice

TAKEHIKO OGUCHI

*Tokyo Institute of Technology, Oh-okayama, Tokyo, Japan*

August 28, 1950

WE have obtained the correlation probabilities,<sup>1</sup> as a measure of the propagation of order in an Ising model of ferromagnetism of the simple cubic lattice, in the form of power series valid at low and high temperatures, respectively. The correlation probability between a spin on the zeroth site and that on the  $n$ th site at a distance of  $n$  sites away in the same line of the crystal from the zeroth site is defined by

$$C(0, n) = f(0, n)/f, \quad (1)$$

where  $f$  is an ordinary partition function and  $f(0, n)$  is a partition function to be taken over the configurations allowed by the restriction by which the spins on zeroth site and  $n$ th site have the same polarities.

For low temperatures, both  $f$  and  $f(0, n)$  are obtained by counting the configurations.<sup>2</sup> Thus, we have found

$$\begin{aligned} C(0, 1) &= 1 - 2\beta^6 - 10\beta^{10} + 14\beta^{12} - 70\beta^{14} + 176\beta^{16} - 626\beta^{18} \dots \\ C(0, 2) &= 1 - 2\beta^6 - 12\beta^{10} + 16\beta^{12} - 88\beta^{14} + 212\beta^{16} - 790\beta^{18} \dots \\ C(0, 3) &= 1 - 2\beta^6 - 12\beta^{10} + 16\beta^{12} - 90\beta^{14} + 216\beta^{16} - 818\beta^{18} \dots \\ C(0, 4) &= 1 - 2\beta^6 - 12\beta^{10} + 16\beta^{12} - 90\beta^{14} + 216\beta^{16} - 820\beta^{18} \dots \end{aligned} \quad (2)$$

and to terms of order  $\beta^{18}$

$$\begin{aligned} C(0, n) &= C(0, 4), & n \geq 5. \\ \beta &= \exp(-2K), & K = J/2kT. \end{aligned} \quad (3)$$

$J$  is the energy gained if two neighbors change from an antiparallel to a parallel position.  $C(0, 1)$  agrees with the one obtained by van der Waerden which is quoted in the paper of Ashkin and Lamb.<sup>1</sup>

For high temperatures the treatment is different from that for low temperatures. The partition function is transformed as follows.

$$f = \sum_{\mu_i = \pm 1} \exp(K \sum_{\langle i, k \rangle} \mu_i \mu_k) = (\cosh K)^{3N} \sum_{\mu_i = \pm 1} \prod_{\langle i, k \rangle} (1 + \mu_i \mu_k \kappa). \quad (4)$$

$$\kappa = \tanh K. \quad (5)$$

where  $\mu_i$  is the spin component on  $i$ th site, which is capable of taking the values,  $+1$  or  $-1$ .  $\sum$  or  $\prod$  means that the sum or product is carried out over all connecting lines between the direct neighbors, and  $\sum_{\mu_i = \pm 1}$  means that the sum is carried out over all spins. (The total number of spins is  $M$ .) In developing the product, we get a series consisting of various products. But after it is summed over all values of the  $\mu_s$ , most of the terms will vanish. The only non-vanishing terms are those which consist of the pairs forming closed polygons in the same way as for the case of the dual transformation.<sup>3</sup> Thus the partition function is expressed in the following form.

$$f = 2^N (\cosh K)^{3N} \left[ 1 + 3N\kappa^4 + 22N\kappa^6 + \left( \frac{9}{2}N^2 + \frac{375}{2}N \right) \kappa^8 \dots \right] \quad (6)$$

and

$$f^{1/N} = 2 (\cosh K)^3 (1 + 3\kappa^4 + 22\kappa^6 + 192\kappa^8 \dots). \quad (7)$$

Equation (7) is the same result as that which D. Ter Haar<sup>4</sup> has obtained by the method of Opechowsky<sup>5</sup> up to terms of order  $K^6$ .

In the expression of  $f(0, n)$ , besides the closed polygons mentioned above, those lines consisting of successive pairs which have their terminals at zeroth spin and  $n$ th spin also contribute as non-vanishing terms. From (1) we have

$$\left. \begin{array}{l} C(0, 1) = \frac{1}{2}(1 + \kappa + 4\kappa^3 + 40\kappa^5 + 456\kappa^7 + 2348\kappa^8 \dots) \\ C(0, 2) = \frac{1}{2}(1 + \kappa^2 + 12\kappa^4 + 176\kappa^6 + 504\kappa^7 + 1156\kappa^8 \dots) \\ C(0, 3) = \frac{1}{2}(1 + \kappa^3 + 24\kappa^5 + 40\kappa^6 + 60\kappa^7 + 84\kappa^8 \dots) \\ C(0, 4) = \frac{1}{2}(1 + \kappa^4 + 40\kappa^6 + 60\kappa^7 + 84\kappa^8 \dots) \\ C(0, 5) = \frac{1}{2}(1 + \kappa^5 + 60\kappa^7 + 84\kappa^8 \dots) \\ C(0, 6) = \frac{1}{2}(1 + \kappa^6 + 84\kappa^8 \dots) \\ C(0, 7) = \frac{1}{2}(1 + \kappa^7 \dots) \\ C(0, 8) = \frac{1}{2}(1 + \kappa^8 \dots) \end{array} \right\} \quad (8)$$

In order to calculate the paramagnetic susceptibility  $\chi$ , we must add the energy due to the external magnetic field  $H$  to the partition function (4). Thus

$$f = \sum_{\mu_i = \pm 1} \exp(K \sum_{\langle i, k \rangle} \mu_i \mu_k + C \sum_i \mu_i) \\ = (\cosh K)^{3N} (\cosh C)^N \sum_{\mu_i = \pm 1} \prod_{\langle i, k \rangle} (1 + \mu_i \mu_k K) \prod_i (1 + \mu_i \tanh C). \quad (9)$$

$$C = mH/kT, \quad (10)$$

where  $m$  is the magnetic moment of each spin. Considering that the susceptibility is proportional to the coefficient of  $(\tanh C)^2$  in  $\log f$ , we obtain

$$\frac{2N\mu^2}{J} \frac{1}{\gamma} = \frac{1}{K} (1 - 6\kappa + 6\kappa^2 - 6\kappa^3 + 30\kappa^4 - 54\kappa^5 + 318\kappa^6 \dots). \quad (11)$$

The theoretical paramagnetic Curie point  $K_p$ , which is obtained from the asymptote of (11), is given by

$$1-6 \tanh K_p=0, \quad K_p=0.168. \quad (12)$$

The results of the ordering influence of more complicated configurations and those of other lattice types will be published in the *Journal of the Physical Society of Japan*.

The author desires to give his sincere thanks to Professors Y. Takagi and R. Kubo for their kind guidance in the course of this work.

- <sup>1</sup> J. Ashkin and W. E. Lamb, Jr., Phys. Rev. **64**, 159 (1943).
- <sup>2</sup> H. A. Kramers and G. H. Wannier, Phys. Rev. **60**, 263 (1941).
- <sup>3</sup> G. H. Wannier, Rev. Mod. Phys. **17**, 50 (1945).
- <sup>4</sup> D. Ter Haar, Phys. Rev. **76**, 176 (1949).
- <sup>5</sup> W. Opechowsky, Physica **4**, 181 (1937).

## The Heat of Dissociation of Carbon Monoxide

GEORGE GLOCKLER

Department of Chemistry and Chemical Engineering,  
State University of Iowa,\* Iowa City, Iowa  
September 5, 1950

September 5, 1950

THE heat of sublimation of carbon  $L(C)$  has been determined lately by three different investigators.<sup>1-3</sup> If in these experiments the equilibrium vapor pressure of carbon is measured, then the atomic heat of dissociation of carbon monoxide  $D_0(CO)$  is about 255 kcal. The ordinary heat of formation<sup>4</sup> of carbon monoxide is 27.2019 kcal. at 0°K, and the heat of dissociation<sup>5</sup> of oxygen molecules is 117.16 kcal.  $D_0(CO)$  must be less than the

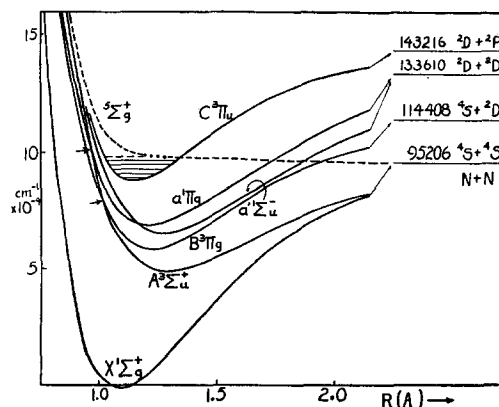


FIG. 1. Energy level diagram of carbon monoxide.

dissociation limit observed from predissociations<sup>8</sup> (11.11 eV) and  $D_0(\text{CO})=11.08$  eV has been adopted, giving less weight to the determination of  $L(\text{C})$  by Marshall and Norton.<sup>3</sup>

The above value of  $D_0(\text{CO})$  has been used to construct the energy diagram of CO shown in Fig. 1. The distinctive feature is a repulsive state arising from  $\text{C}(^3P)+\text{O}(^3P)$  at  $89397\text{ cm}^{-1}$  or  $11.08\text{ eV}$  and reaching about  $89700\text{ cm}^{-1}$  or  $11.12\text{ eV}$  at  $r=1.2\text{ \AA}$ . Toward smaller distances it rises and at  $1.1\text{ \AA}$  it is about  $93500\text{ cm}^{-1}$  or  $11.60\text{ eV}$ . This repulsive level is supposed to predissociate  $\text{C}^2\Sigma^+$  ( $v=0, K=29$ ) at  $93536\text{ cm}^{-1}$ ,  $\text{B}^2\Sigma^+$  ( $v=0, K=38$ ) at  $89700\text{ cm}^{-1}$ ,  $\text{B}^2\Sigma^+$  ( $v=1, K=18$ ) at  $89650\text{ cm}^{-1}$ , and  $\text{b}^2\Sigma^+$  ( $v=0, K=55$ ) at about this height. The vibration levels  $v=1$  of  $\text{C}^2\Sigma^+$  ( $\sim 94008\text{ cm}^{-1}$ ),  $v=2$  of  $\text{B}^2\Sigma^+$  ( $\sim 90940\text{ cm}^{-1}$ ) are affected by the crossing of this assumed repulsive state and no bands arising from them have been found as yet.<sup>7</sup> The repulsive state may perhaps cause the effects observed, not only by predissociation but also by dissociating molecules possessing energies in this region by virtue of a greater transition probability. All other irregularities in the spectrum of CO are considered to be perturbations.  $\text{A}'\Pi$  is an example.<sup>8</sup> The state  $\text{b}^2\Sigma^+$  ( $v=2$ ) at about  $88140\text{ cm}^{-1}$  is crossed by  $\text{a}^3\Sigma^+$  at  $r=1.02\text{ \AA}$  leading to strong perturbation which may be the reason for its absence at that point.<sup>8</sup>

It is suggested that this energy diagram can serve as a start to explain all perturbations and so-called predissociations of the CO molecule provided the simple Morse curves are replaced by others involving the rotational changes mentioned by Oldenberg.<sup>9</sup>

\* Financial support was received from ONR under Contract N-8 onr 79400.

<sup>1</sup> Brewer, Gilles, and Jenkins, *J. Chem. Phys.* **16**, 797 (1948).

<sup>2</sup> Simpson, Thorn, and Winslow, AEC Argonne National Laboratory, Report of Chemistry Division ANL-4264 (1949).

<sup>3</sup> A. L. Marshall and F. J. Norton, *J. Am. Chem. Soc.* **72**, 2166 (1950).

<sup>4</sup> *Selected Values of Properties of Hydrocarbons* (National Bureau of Standards, Circular C461, 1947).

<sup>5</sup> G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950).

<sup>6</sup> A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (John Wiley and Sons, Inc., New York, 1947).

<sup>7</sup> References 5 and 6 give all of the literature references used.

<sup>8</sup> Reference 6, p. 186.

<sup>9</sup> O. Oldenberg, *Zeits. f. Physik* **56**, 563 (1929).

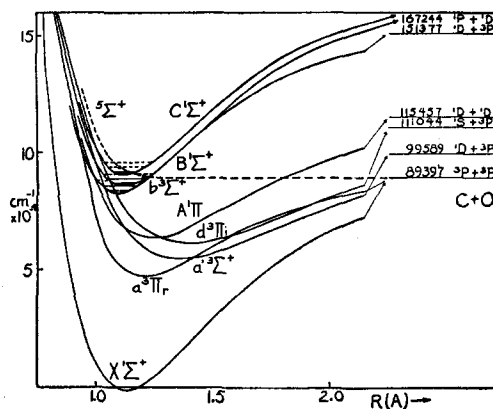


FIG. 1. Energy level diagram of nitrogen.

for CO] do not follow this rule. However, the term  $\text{a}'(^1\Sigma_u^-)$  for  $\text{N}_2$  can be calculated to be  $66380\text{ cm}^{-1}$  from  $\text{d}^3\Pi_u$  ( $62299.4$ ) of CO. Gaydon estimates it to be around  $65000$  to  $67000\text{ cm}^{-1}$ . Applying the rule to  $D(\text{N}_2):D(\text{CO})$  with  $D(\text{CO})=11.08\text{ eV}$  yields  $D(\text{N}_2)=11.80\text{ eV}$ . This value has been used to construct an energy diagram for nitrogen (Fig. 1). It is supposed that a repulsive state starts from the  $^4S+^4S$  level ( $95206\text{ cm}^{-1}$ ) and crosses  $\text{C}^3\Pi_u$  just below  $97946\text{ cm}^{-1}$  at the dissociation limit.<sup>2,3</sup> The breaking-off points on account of predissociation in  $v'=1, 2, 3, 4$  at  $K=65, 55, 43$ , and  $28$  lie on this repulsive curve at about  $1.195, 1.223, 1.253$ , and  $1.281\text{ \AA}$ , respectively. These points were found from the work of Büttendörfer and Herzberg<sup>5</sup> and sketching the probability functions of the oscillator onto the corresponding vibration levels. It may be that this proposed repulsive state has a greater transition probability than other states at about  $11\text{ eV}$  and hence other states may not appear. The  $\text{A}^3\Sigma_u^+$ -state perturbs  $\text{B}^3\Pi_g$  ( $v=12$ ) at  $79385$  and the  $\text{a}'\Pi_u$  ( $v=9$ ) at  $84787\text{ cm}^{-1}$ . In Fig. 1 these crossings happen at  $74000$  and  $98000$ , respectively. It must be remembered that these simple Morse curves do not give quite the correct picture of the potential energy of the molecule. It is suggested that the value  $D(\text{N}_2)=11.8\text{ eV}$  mentioned here deserves consideration and that this diagram can serve as basis for explaining all the perturbations and so-called predissociations of the nitrogen molecule. An early value of  $D(\text{N}_2)=11.5\text{ eV}$  by Sponer<sup>6</sup> was based on electron impact experiments and hence less accurate. The possibility that active nitrogen is really nitrogen atoms must again be considered.<sup>7</sup>

\* Financial support was received from ONR under Contract N-8 onr 79400.

<sup>1</sup> K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (Verlag, Julius Springer, Berlin, 1931).

<sup>2</sup> G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950).

<sup>3</sup> A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (John Wiley and Sons, Inc., New York, 1947).

<sup>4</sup> Reference 3, p. 184.

<sup>5</sup> G. Büttendörfer and G. Herzberg, *Ann. d. Physik* **21**, 577 (1935).

<sup>6</sup> H. Sponer, *Zeits. f. Physik* **34**, 622 (1925).

<sup>7</sup> R. J. Strutt, *Proc. Roy. Soc.* **85**, 219 (1911).

## The Heat of Dissociation in Nitrogen

GEORGE GLOCKLER

Department of Chemistry and Chemical Engineering,  
State University of Iowa,\* Iowa City, Iowa

September 5, 1950

AN estimate of the heat of dissociation of nitrogen is made by comparing this molecule with the isoelectronic carbon monoxide. The force constants<sup>1</sup> are  $k(\text{N}_2)=2.29$  and  $k(\text{CO})=1.89$  megadynes/cm. The internuclear distances<sup>2</sup> are  $R(\text{N}_2)=1.095\text{ \AA}$  and  $R(\text{CO})=1.128\text{ \AA}$ . The currently discussed heats of dissociation<sup>2,3</sup> are  $D(\text{N}_2)=9.764$  or  $7.384\text{ eV}$  and  $D(\text{CO})=9.61$  or  $11.1\text{ eV}$ . The latter value fits the determinations of the heat of sublimation of carbon<sup>4</sup> (preceding note). From a comparison of these properties one would expect that the heat of dissociation of nitrogen should also be greater than either of the above values. If the term values of  $\text{N}_2$  are compared with the ones of CO arranged in order of magnitude,<sup>2</sup> then it is found that they stand in the ratio  $1.0655:1$ . The second highest terms [ $\text{A}^3\Sigma_u^+$  ( $50206$ ) for  $\text{N}_2$  and  $\text{a}^3\Pi_r$  ( $48688$ )