

THE HEAT OF DISSOCIATION OF THE CARBON MONOXIDE MOLECULE AND THE HEAT OF SUBLIMATION OF CARBON¹

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There has recently been a great deal of discussion on the value of the heat of dissociation of the carbon monoxide molecule, $D(\text{CO})$. Various widely diverging values have been given as more or less definite for this quantity by different investigators. All these values have been obtained by spectroscopic methods. The discrepancies in the case of carbon monoxide seem to throw a rather unfavorable light on the reliability of these spectroscopic methods, and the non-spectroscopist may even doubt their accuracy and reliability in other cases where the spectroscopic values claim to be perfectly certain and have been generally accepted. In the first part of this paper we shall, therefore, summarize the various spectroscopic methods, emphasizing under what conditions they supply reliable values for the heats of dissociation, D . In the second part, these methods will be applied to carbon monoxide as far as possible. The various spectroscopic values for $D(\text{CO})$ proposed in the literature will be discussed, possible reasons for the discrepancies will be pointed out, and a value which seems most probable to the author will be given.

The value of $D(\text{CO})$ is rather important in the discussion of many chemical problems. Particularly the heat of sublimation of carbon into normal atoms L_1 may be derived from $D(\text{CO})$. L_1 in its turn is necessary for the calculation of atomic heats of formation and bond energies of carbon compounds. Therefore a discussion of the heat of sublimation of carbon is added, as well as a brief discussion of the dissociation energy of the CN radical, which also may be derived from $D(\text{CO})$.

I. SPECTROSCOPIC METHODS FOR THE DETERMINATION OF HEATS OF DISSOCIATION OF DIATOMIC MOLECULES

In forming a molecule the atoms may be brought together in any of their excited states, including of course the normal state. From each of

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the combinations of the excited atoms in general *several* electronic states of the molecule arise. The different electronic states belonging to the same combination of atomic states have different potential energy curves, some with a minimum of potential energy (stable states) and some without it (unstable repulsive states). The difference in energy of the zero vibrational level of an electronic state and the asymptote of the potential curve is the dissociation energy of that state. The energy corresponding to the asymptote is also called the *dissociation limit*. There are as many different dissociation limits as there are combinations of the different states of the two atoms. The distance of the lowest dissociation limit which corresponds to dissociation into normal atoms from the ground state of the molecule is called the *dissociation energy of the molecule*. This is the quantity in which the chemist is most interested. Usually (but not necessarily) the ground state of the molecule is derived from normal atoms, i.e., the dissociation energy of the ground state is the dissociation energy of the molecule.

There are always two steps in the spectroscopic determination of this quantity: (A) the determination of one or preferably more of the dissociation limits of the molecule; (B) the determination of the products of dissociation, i.e., of the states in which the atoms are at the dissociation limits which have been found. The discrepancies which occur in the literature are mostly caused by a mistake or ambiguity in the second step.

A. Determination of dissociation limits

There are four possible ways of performing step A, i.e., of determining dissociation limits from band spectra.

Method a. The oldest method, due to Franck, is that of the *convergence limits* of band series. If the molecule goes over from the vibrationless ground state to the various vibrational levels of an upper electronic state, a series of bands is observed in the absorption spectrum, somewhat as in figure 1.

The distance of successive bands decreases towards shorter wave lengths until it reaches the value zero at a certain limit, the convergence limit, where a continuous spectrum follows to still shorter wave lengths. This continuous spectrum means, as has been rigorously proved both experimentally and theoretically, a dissociation of the molecule. The beginning of the continuous spectrum, i.e., the convergence limit, corresponds to the beginning of dissociation, i.e., the dissociation limit.

Figure 2 shows the potential curves of the upper and lower state in a case like this. Absorption of light in the continuous region means dissociation with a certain amount of kinetic energy, corresponding in magnitude to the distance from the convergence limit.

If a convergence limit like this is actually observed for a certain molecule, at once a very accurate and reliable value for the corresponding dissociation limit can be given.² This method has been applied very successfully to I_2 , O_2 , H_2 , and others. Unfortunately, many diatomic molecules do not exhibit a suitable absorption spectrum, therefore other methods have to be applied to them.

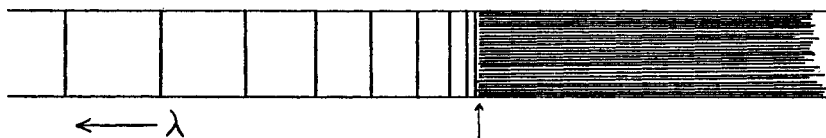


FIG. 1. Band series with convergence limit and continuous spectrum (schematically)

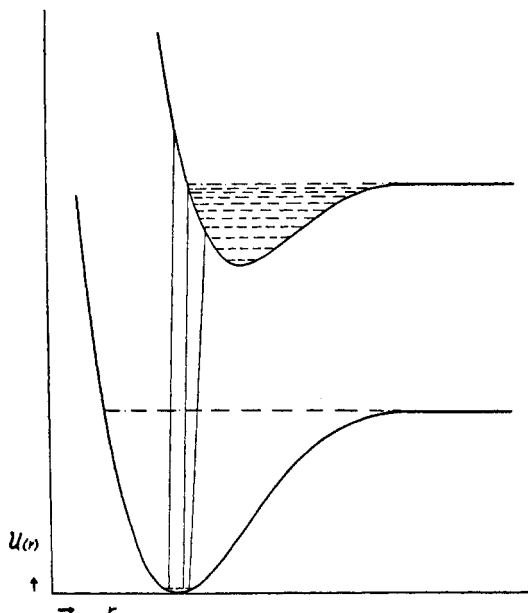


FIG. 2. Potential curves for figure 1

Method b. It often happens that not the complete series of absorption bands up to the point of convergence and the continuum are observed, but

² There is a remote possibility that under certain very special circumstances the potential curve of the upper state has a maximum before approaching the asymptote. In that case the observed limit in the absorption spectrum would correspond to an energy greater than the dissociation limit. So far no such case has been observed with certainty. Also, it would be possible to distinguish it from the ordinary case, figure 2, so that we need not discuss it here.

only the first few bands corresponding to the first vibrational levels of the upper state. Similarly in emission usually only transitions between the lower vibrational levels are observed. The reason for this is given by the Franck-Condon principle (24, 37). As the distance between the vibrational levels, i.e., the distance of the corresponding bands in general decreases regularly, Birge and Sponer have proposed to *extrapolate* the series of the observed quanta to zero and then add all the vibrational quanta to obtain the heat of dissociation of the state in question. The advantage of this procedure is that it may be applied to any electronic state of a molecule for which a number of vibrational levels are known.

However, it has been found in recent years that the results of this method are often not at all accurate. In some cases the true values obtained by other methods deviate from the extrapolated values by as much as 40 per cent. The error is much smaller if the extrapolation is comparatively short. In most of the cases which have been tested so far the extrapolated value was higher than the true value, so that one may say that the extrapolations according to Birge and Sponer, in general give an upper limit for the heat of dissociation of a particular electronic state of the molecule, whereas, of course, the sum of the actually observed vibrational quanta always gives a lower limit for it. The knowledge of this lower limit, which is quite definite, may sometimes be of help in the discussion of dissociation energies.

Method c. Sometimes in absorption only a continuous spectrum is observed. This either corresponds to the transitions to the continuous part of a stable electronic level, the discrete part being not observed owing to the Franck-Condon principle, or to the transition into an unstable repulsive electronic state. Evidently the long wave length limit of this continuum gives a definite upper limit for the dissociation energy of the molecule.³ But an accurate value for the dissociation limit cannot be derived because the point of convergence cannot be located. In fact the upper limit derived from the long wave length limit of the continuum may be and in some cases has actually been found to be appreciably higher than the true value.

Instead of using the continuous absorption as an indication of dissociation, Terenin has used the occurrence of fluorescence of the atoms produced if the dissociation takes place into excited atoms. As this is not important for the discussion of carbon monoxide we shall not deal with this method in more detail.

Method d. A method which under certain conditions also gives very

³ This refers to adsorption at sufficiently low temperatures, where absorption due to molecules in higher vibrational levels of the ground state does not interfere.

reliable results, just as method a, is the determination of dissociation limits by *predissociation*.⁴

Predissociation was discovered by V. Henri when he investigated the absorption spectra of a number of molecules. He found in some cases that though the absorption bands are quite sharp at longer wave lengths, they become diffuse more or less suddenly at a certain point and sometimes get sharp again at shorter wave lengths.

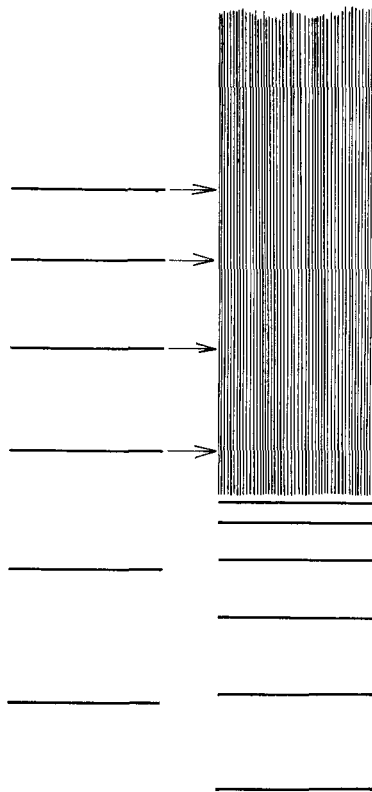


FIG. 3. Radiationless transitions (predissociation) from a discrete to a continuous state

This diffuseness was shown by Born, Franck, Kronig, and others, to be due to an instability of the molecule. Namely, if the upper level of the bands has a larger energy than a dissociation limit of the molecule, it is overlapped by the continuous term spectrum which extends beyond this dissociation limit, as indicated in figure 3. Owing to quantum-mechanical

⁴ For a more complete discussion of this, see the author's review on predissociation (17).

resonance, there is then a certain probability that the molecule performs a radiationless transition (indicated by horizontal arrows in figure 3) from the discrete excited state to the continuous term spectrum, and this under certain conditions, as shown by the theory, produces the diffuseness which is observed. It follows immediately that the *predissociation limit*, i.e., the beginning of the diffuseness of the bands, gives an upper limit to the dissociation energy of the molecule.

It has been shown experimentally, first by Bonhoeffer and Farkas, that a dissociation of the molecule really does occur if light of the diffuse absorption bands is absorbed. Moreover, it was found, as is to be expected on this theory of radiationless dissociation, that bands which have the diffuse states as upper states do not occur in emission, whereas the other bands of the same system do. Thus there are three possible tests for predissociation: diffuseness of absorption bands, actual dissociation, and quenching of emission bands.

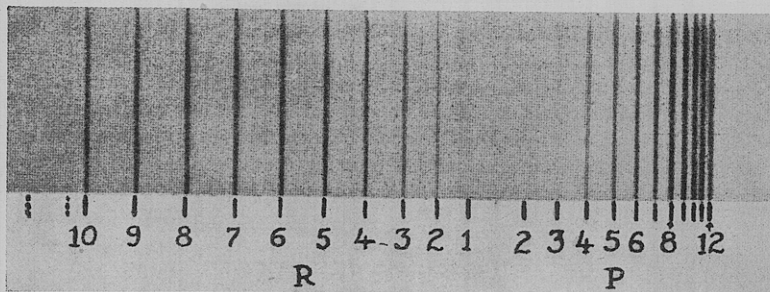


FIG. 4. Breaking off (predissociation) in the CaH band at 3533.6 Å. U., according to Mulliken

In order to produce a detectable diffuseness in the absorption bands, the radiationless transition probability must be at least ten to one-hundred times larger than the transition probability for radiation, whereas to produce a detectable quenching, it is sufficient that the two transition probabilities be of about the same magnitude.⁴ Therefore, quenching of emission bands is a much more sensitive test for predissociation. Also, it can be applied to detect predissociation in electronic states of a molecule which cannot be investigated by absorption.

The quenching of emission bands due to predissociation is usually detected by an abrupt breaking off of the band spectrum at a certain value a of the vibrational quantum number, v' , of the upper state. Bands having $v' > a$ do not occur at all or only much weaker than those with $v' \leq a$. In many cases if the rotational fine structure of the bands is resolved, it is even found that the break occurs between successive rotational levels of

the last vibrational level $v' = a$. Figure 4 gives as an example an emission band of CaH, where the breaking off in the two branches (on the extreme left and extreme right) can be clearly seen. Lines with the rotational quantum number of the upper state $K' > 11$ are completely missing, whereas lines with $K' \leq 11$ have the ordinary intensity. In some cases, only a sudden drop in intensity is observed instead. Evidently the predissociation limit can be fixed with considerable accuracy if such a breaking off of the rotational fine structure is observed.

In principle, predissociation in an excited state of a molecule is possible as soon as its energy is larger than the energy necessary to dissociate the molecule into normal atoms. But, just as for transitions with radiation, there are also selection rules for radiationless transitions, and in consequence of that in some cases a predissociation may not be possible into normal atoms, but only into excited atoms.

In order to formulate the selection rules, it has to be remembered that the unstable state into which the radiationless transition occurs is nevertheless a molecular state, also characterized by the various molecular quantum numbers and symmetry properties. According to Kronig, a radiationless transition can only occur between states which have the same symmetry properties, and for which $\Delta S = 0$, $\Delta J = 0$, and $\Delta \Lambda = 0$ or $+1$ or -1 . The rule $\Delta S = 0$ is the ordinary intercombination rule, which holds to the same extent as for ordinary transitions with radiation. The other rules will not be discussed here in detail because we do not need them for the following.

In addition to the Kronig rules, the Franck-Condon principle has to be considered.⁴ In consequence of that, in general predissociation will only occur if the potential curves of the two states involved intersect. The point of intersection may be (a) at about the same height as the asymptote of the state into which predissociation takes place or (b) below it or (c) above it. This is shown in figure 5. In the cases a and b, a predissociation, i.e., a going over from potential curve α to α' will occur as soon as the energy is larger than that of the asymptote. Consequently the predissociation limit is equal to the dissociation limit of the molecule. However, in case c, where the point of intersection is above the asymptote, predissociation can only occur for vibrational levels above this point of intersection.⁵ Therefore, in this case the predissociation limit is larger than the corresponding dissociation limit. Only if it is possible to exclude this case c for an observed predissociation, can a dissociation limit be

⁵ As we have to do with motions of heavy nuclei, the quantum-mechanical tunnel effect produces a detectable going over from α to α' in figure 4c only immediately below the top of the potential hill formed by the two curves. This can be neglected here. (Cf. reference 18.)

accurately determined from the predissociation limit. In all other cases, predissociation limits only give upper limits for dissociation limits.

The above-mentioned possibility of excluding case c exists if a breaking off of the rotational levels is observed not only in one but in two or more successive vibrational levels (18, 19a). Evidently, if in the last vibrational level $v' = a$ the breaking off occurs for a low value of the rotational

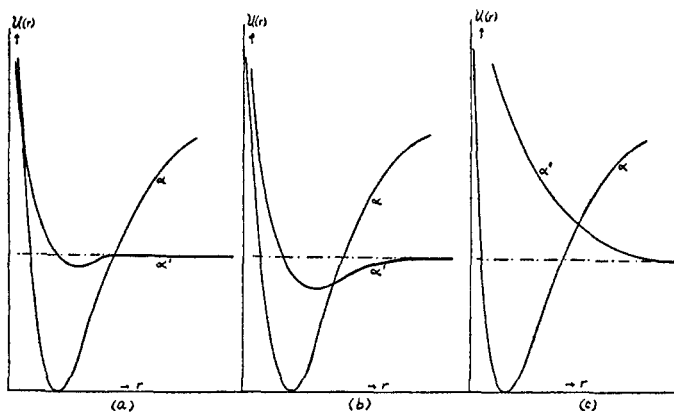


FIG. 5. The three different cases of predissociation

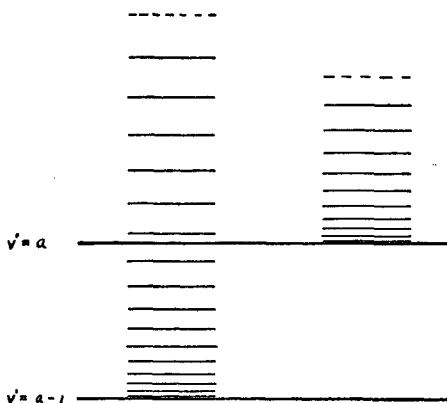


FIG. 6. Breaking off in two successive vibrational levels

quantum number K there may also be a breaking off in the level $v' = a - 1$ at a correspondingly higher K value, as indicated in figure 6. Owing to the influence of the centrifugal force, the breaking off occurs at a slightly higher energy in the level $v' = a - 1$ than in the level $v' = a$. Theory shows that only if this difference in energy is small compared to the difference of the pure rotational energies of the two levels, does case c not

apply, i.e., the predissociation limit is very near to the dissociation limit. In fact, even a lower limit for the latter may be obtained in this case, so that it is included between two rather close limits. Under these conditions, but only then, is it possible to derive very reliable and accurate values for dissociation limits from predissociation data. In all other cases the latter give only upper limits for dissociation limits.

If the intensity drop occurs only for a few consecutive fine-structure lines in emission, it is, except in special cases, due to *perturbation*, not ordinary predissociation. Perturbations arise by a sort of resonance if two discrete levels of the molecule have very nearly the same energy. This leads to a shift of the energy levels from their original position and, at the same time, to a change in intensity of the corresponding fine-structure lines. If, therefore, the lines with low intensity at the same time have not their regular position, the drop in intensity has nothing to do with predissociation. But sometimes, e.g., in some N_2 bands (7), an intensity drop for a few lines is observed without corresponding frequency shift. This was explained by Ittmann (23) as *accidental predissociation*, i.e., a perturbation for which the perturbing term is a predissociating term at the same time. In this case the intensity drop, as for ordinary predissociation, is due to a dissociation of the molecule, not however by a direct radiationless transition to the unstable state, but by first going over to another discrete state which then predissociates. This explains at once the fact that an intensity drop occurs only for very few consecutive rotational states, just as for ordinary perturbations but without noticeable frequency shift. Though this is so far the only experimental proof for accidental predissociation, it seems fairly safe to assume the correctness of this interpretation of intensity drops for a few consecutive lines without frequency shift. It is evident from the foregoing that an observed accidental predissociation gives an upper limit for a dissociation limit but not more, whereas ordinary perturbations of course have nothing to do with dissociation limits.

B. Determination of the products of dissociation

The values for the dissociation limits obtained by any of the methods a, b, c, or d in general correspond to dissociation into more or less excited atoms. In order to determine the dissociation energy of the molecule, the state of excitation of the atoms produced at the observed dissociation limit has to be determined. If that is not possible, the observed dissociation limits, even if they are accurate, are only upper limits for the dissociation energy of the molecule which is smaller by the excitation energy of the products of dissociation (cf. figure 2).

Information about the products of dissociation for a certain dissociation limit may be obtained in three ways:

(1). By comparing its energy with that of other dissociation limits of the same molecule (or the corresponding molecule ion). Evidently the differences in energy of the various dissociation limits must equal the energy differences of the two free atoms forming the molecule.

(2). By application of the Wigner–Witmer *correlation rules* (30). These rules give the number and type of the molecular terms which can arise from each combination of terms of the two atoms forming the molecule, e.g., an atom in a 2S state and one in a 3P state can give only the molecular states ${}^2\Sigma$, ${}^2\Pi$, ${}^4\Sigma$, ${}^4\Pi$ and no others; two equal atoms both in a 3P state give the molecular states ${}^1\Sigma_g^+$, ${}^1\Sigma_g^+$, ${}^1\Sigma_u^-$, ${}^1\Pi_g$, ${}^1\Pi_u$, ${}^1\Delta_g$, ${}^3\Sigma_u^+$, ${}^3\Sigma_u^+$, ${}^3\Sigma_g^-$, ${}^3\Pi_u$, ${}^3\Pi_g$, ${}^3\Delta_u$, ${}^5\Sigma_g^+$, ${}^5\Sigma_g^+$, ${}^5\Sigma_u^-$, ${}^5\Pi_g$, ${}^5\Pi_u$, ${}^5\Delta_g$ and similarly in other cases. The Wigner–Witmer rules are derived from pure symmetry considerations and are therefore strictly valid.⁶

(3). In special cases by observation of atomic fluorescence when the molecule has been irradiated with light that produces dissociation of the molecule into one excited and one normal atom. The emitted atomic line of course indicates the excitation energy of the atom on dissociation. This method was first applied by Terenin. It will not be used in the following considerations.

For a better understanding of methods 1 and 2 let us consider two examples, the determination of the heats of dissociation of O_2 and N_2 .

In O_2 a convergence limit was observed in the absorption spectrum at 1770 A.U., corresponding to an energy of 7.01 volts.⁷ There are three low-lying terms of the oxygen atom (8, 22), 3P (ground state), 1D (1.957 volts), 1S (4.168 volts), which have to be considered as dissociation products at the limit 7.01 volts.⁸ The two oxygen atoms may therefore be in the states ${}^3P + {}^3P$ or ${}^3P + {}^1D$ or ${}^3P + {}^1S$ or ${}^1D + {}^1D$ or ${}^1D + {}^1S$ or ${}^1S + {}^1S$. The upper state of the absorption bands which lead to the convergence is a ${}^3\Sigma_u^-$ state, as shown by the fine-structure analysis. Such a state, according to the Wigner–Witmer rules, cannot dissociate into two normal 3P atoms (see the previous example) (15). Similarly the three combinations ${}^1D + {}^1D$, ${}^1D + {}^1S$, and ${}^1S + {}^1S$ are excluded because they do not give triplet states at all. The two remaining possibilities, ${}^3P + {}^1D$ and ${}^3P + {}^1S$, would give $7.01 - 1.96 = 5.05$ volts and $7.01 - 4.17 = 2.84$

⁶ For heavy molecules sometimes Hund's case *c* applies. The adaption of the Wigner–Witmer rules to this case has been given by Mulliken (30).

⁷ This is the new value given by Knauss and Ballard (25), which is based on spectrograms of much higher dispersion than the previous value, 7.05 volts.

⁸ The next highest term of oxygen is 9.1 volts above the ground level. If one of the dissociation products were in that state, a negative value for *D* would result.

volts, respectively, for the dissociation energy of oxygen. The latter value is smaller than the sum of the observed vibrational levels of the ground state, 3.4 volts. Thus the value 5.05 volts = 116.4 kg-cal. per mole for $D(\text{O}_2)$ follows without ambiguity. In fact, a second convergence limit was later found (19) at 5.09 volts, corresponding to dissociation into normal atoms $^3P + ^3P$. The distance between the two convergence limits is 1.92 volts, which is equal to the excitation energy of the 1D level within the splitting of the 3P ground state.⁹ Thus the previous conclusion that the upper convergence limit corresponds to a dissociation into $^3P + ^1D$ is confirmed and the reliability of the method shown. The spectroscopic $D(\text{O}_2)$ value is now absolutely certain, and much more accurate than any thermal or chemical value hitherto obtained.

For N_2 predissociation has been observed in the $C^3\Pi_u$ and in the $B^3\Pi_g$ states (16, 20, 7, 40). By the method indicated previously the predissociation in $C^3\Pi_u$ leads to a reliable value for a dissociation limit at 12.08 volts (16, 20, 7), whereas from the predissociation in the $B^3\Pi_g$ state it is only possible to give an upper limit of 9.79 volts for the corresponding dissociation limit. The low-lying states of the nitrogen atom are 4S (ground state), 2D (2.368 volts), 2P (3.553 volts). As possible products of dissociation we have $^4S + ^4S$ or $^4S + ^2D$ or $^4S + ^2P$ or $^2D + ^2D$ or $^2D + ^2P$ or $^2P + ^2P$. A closer examination of the lower predissociation at 9.79 volts shows that the unstable state producing the predissociation must be a Π or a Δ state,¹⁰ a state which, according to the Wigner-Witmer rules, cannot be obtained from $^4S + ^4S$. The other possibilities for the dissociation products at this limit give the following upper limits for $D(\text{N}_2)$: ≤ 7.42 or ≤ 6.24 or ≤ 5.05 or ≤ 3.87 or ≤ 2.68 volts. The last three values are definitely excluded by the fact that the energy of the last observed vibrational level of the ground state has the energy 5.5 volts. Also the value $D(\text{N}_2) \leq 6.24$ volts seems to be extremely improbable on this basis, so that we have $D(\text{N}_2) \leq 7.42$. A more accurate value can be obtained by making use of the upper predissociation in the $C^3\Pi_u$ state which gave an exact value for a dissociation limit (=12.08 volts). If $D(\text{N}_2)$ is between 7.42 and 6.24 volts the upper predissociation must correspond to a dissociation into $^2D + ^2D$, so that we have $D(\text{N}_2) = 12.08 - 2 \times 2.368 = 7.345$ volts = 169.3 kg-cal. per mole (21; 20). The remote

⁹ The difference between the distance 1.92 volts of the two dissociation limits and the energy difference 1.96 volts of the ground state 3P_2 of the oxygen atom and the 1D state is evidently due to the fact that at the lower dissociation limit not two normal 3P_2 atoms are obtained, but $^3P_2 + ^3P_0$ or $^3P_1 + ^3P_0$, which corresponds to an energy difference of 0.03 or 0.05 volt, respectively.

¹⁰ A Σ state could, so to speak, only predissociate half of the $B^3\Pi_g$ state, and in consequence of that not all of the three branches of a band could show the breaking off as they actually do.

possibility that predissociation at 12.08 volts takes place into ${}^2D + {}^2P$ and therefore that $D(N_2) = 6.18$ volts is completely ruled out by further data on N_2 , which we are not going to discuss here (31). Thus the above value for $D(N_2)$ is also quite definite and very accurate (± 0.005 volt).

II. APPLICATION TO THE CARBON MONOXIDE MOLECULE

Turning now to the carbon monoxide molecule, we first discuss step A, i.e., the determination of dissociation limits. So far no convergence limit is known for carbon monoxide. Extrapolations of the vibrational levels

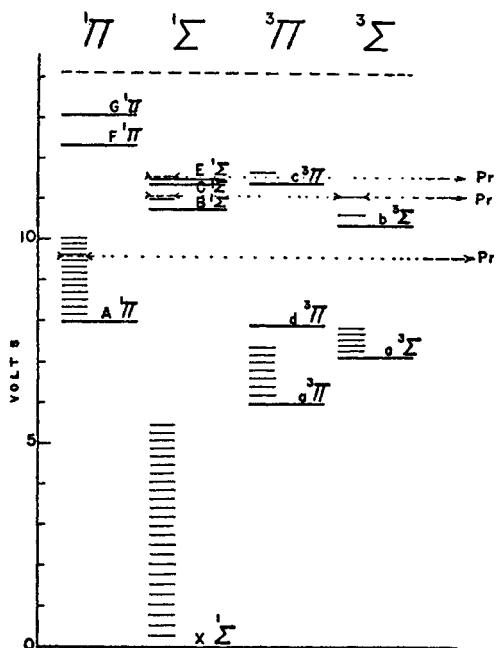


Fig. 7. Energy level scheme of carbon monoxide

of several electronic states have been made in previous years, but, as pointed out above, no reliable D values can be expected from them. It could, however, be concluded that $D(CO)$ is comparatively large, of the order of 10 volts.

Most of the recent discussion of $D(CO)$ is based on predissociation data. Predissociation has been found in four different electronic states of the molecule. The energy level diagram of the carbon monoxide molecule is given in figure 7. The points of predissociation are indicated by "Pr."

The first to discover a predissociation of the carbon monoxide molecule were Coster and Brons (6). They found a sudden drop of intensity in

the 0-1 Ångström band ($B^1\Sigma \rightarrow A^1\Pi$) at $K' = 38$. From their published photometer curve this sudden decrease in intensity can be very clearly seen. All the following lines have a much smaller intensity than those before the break. As they do not, however, vanish completely, the radiationless transition probability for some reason is rather low. Schmid and Gerö (34) found a second breaking off in the $v' = 1$ level of the $B^1\Sigma$ state at $K' = 18$. From this the corresponding dissociation limit can be calculated in the same way as in the case of N_2 previously mentioned (cf. 32). A value of $89,620 \pm 50 \text{ cm.}^{-1} = 11.054 \text{ volts}$ is obtained.¹¹

Schmid and Gerö (9, 35, 12) found a second predissociation in the $v' = 1$ and $v' = 0$ levels of the $b^3\Sigma$ state (upper state of the third positive group). It turns out that this predissociation belongs to the same dissociation limit, so that it need not be discussed further.¹²

A third predissociation was found in the $v = 0$ level of the $C^1\Sigma$ state by Schmid and Gerö (36, 33). The energy of this predissociation limit is $93,550 \text{ cm.}^{-1} = 11.538 \text{ volts}$. As in this case predissociation is only observed in one vibrational level, the value given represents only an upper limit for the corresponding dissociation limit.

Fourthly, predissociation has been found in the $A^1\Pi$ state of carbon monoxide. At first Brons (4) thought that he had located a predissociation in the $v = 10$ level of this state at 9.66 volts above the ground state. But the unreality of this predissociation was soon proved by Gerö (10). According to him the apparent sudden intensity decrease observed by Brons is due to an ordinary perturbation and insufficient exposure time. However, Gerö (11) found another predissociation in the same band system for bands with $v' = 9, 8, \text{ and } 7$. From this he derives in the manner described above a dissociation limit at $77,497 \pm 44 \text{ cm.}^{-1} = 9.558 \text{ volts}$. The intensity drop in the 9-18 band reproduced by Gerö is only slight and extends only over two or three successive rotational lines. This suggests that it may not be an ordinary predissociation but a case of accidental predissociation (cf. above) or even of ordinary perturbation. The same may be true for the drop in the levels $v' = 8$ and 7 , which has only been observed in the R branches of two and one bands respectively. To the writer it seems most probable that we have here a case of accidental predissociation, and that therefore the above value is only an upper limit for the corresponding dissociation limit. But the other two possibilities—ordinary predissociation and ordinary perturbation—have also to be considered. The former would mean that 9.558 volts is a real dissociation

¹¹ This is the value given by Gerö (11).

¹² Lessheim and Samuel (26) have used the fact that no higher vibrational levels are observed in the $b^3\Sigma$ state to derive an upper limit for $D(\text{CO})$, but have not taken account of the observed amount of rotational energy.

limit, whereas the latter would mean that there is no dissociation limit at this energy.

We have thus to deal with the three limits: $93,550 \text{ cm.}^{-1} = 11.538 \text{ volts}$, $89,620 \text{ cm.}^{-1} = 11.054 \text{ volts}$, and $77,497 \text{ cm.}^{-1} = 9.558 \text{ volts}$, of which the first is only an upper limit for a dissociation limit, the second is equal to a dissociation limit, and the third probably is only an upper limit for a dissociation limit, but may also be equal to it or even may not be real.

As we have the most definite data about the predissociation at 11.054 volts, and as this is equal to a dissociation limit, it seems best to start the discussion of the products of dissociation with it.

TABLE 1
D(CO), L, and D(CN) values for different assumptions about the products of dissociation at the carbon monoxide dissociation limit, 11.054 volts

DISSOCIATION PRODUCTS AT 11.054 VOLTS		ATOMIC EXCITATION ENERGY*		D(CO)			L ₁	D(CN)	
Carbon	Oxygen	cm. ⁻¹	Volts	cm. ⁻¹	Volts	kg-cal.	kg-cal.	Volts	kg-cal.
³ P	³ P	0	0	89,620	11.054	254.8	169.2	7.87	181.4
¹ D	³ P	10,192	1.257	79,428	9.797	225.8	140.2	6.61	152.4
³ P	¹ D	15,868	1.957	73,752	9.097	209.7	124.1	5.91	136.3
¹ S	³ P	21,647	2.670	67,973	8.384	193.3	107.7	5.20	119.9
¹ D	¹ D	26,060	3.214	63,560	7.840	180.7	95.1	4.66	107.3
³ P	¹ S	33,793	4.168	55,827	6.886	158.7	73.1	3.70	85.3
⁵ S	³ P	34,994	4.32	54,626	6.738	155.3	69.7	3.55	81.9
¹ S	¹ D	37,515	4.627	52,105	6.427	148.1			
¹ D	¹ S	43,985	5.425	45,635	5.629	129.8			
⁵ S	¹ D	50,862	6.273	38,758	4.781	110.2			
¹ S	¹ S	55,440	6.838	34,180	4.216	97.2			
⁵ S	¹ S	68,787	8.484	20,833	2.570	59.2			

* The lowest component of the ³P terms has always been chosen.

The lowest states of the oxygen atom are ³P (ground state), ¹D (1.957 volts), ¹S (4.168 volts); those of the carbon atom, ³P (ground state), ¹D (1.257 volts), ¹S (2.670 volts) and ⁵S (4.32 volts, not yet observed; the value given was theoretically calculated by Bacher and Goudsmit (2)). Combining each of these states of the carbon atom with each of the states of the oxygen atom gives twelve possibilities as dissociation products at the 11.054 volts dissociation limit. These are given¹³ in the order of their energy in the first two columns of table 1. The next two columns give the excitation energy above the normal state ³P + ³P in cm.⁻¹ and volts. In order to get D(CO) the excitation energy of the dissociation products has

¹³ A similar but less complete table has also been given by Goldfinger, Lasareff, and Rosen (14).

to be subtracted from the energy of the dissociation limit, 11.054 volts. The resulting $D(\text{CO})$ values corresponding to the dissociation products of columns 1 and 2 are given in columns 5, 6, and 7 in cm.^{-1} , volts, and kg-cal. per mole . Of these twelve possible values for $D(\text{CO})$ one has to try to exclude eleven in order to come to a definite value for this quantity.

In the ground state of carbon monoxide twenty-five vibrational levels have been observed so far, the highest one having an energy of about $45,000 \text{ cm.}^{-1} = 5.6$ volts. This is definitely a lower limit¹⁴ for $D(\text{CO})$. In fact, considering the slow and quite regular decrease of the observed vibrational quanta (from 2142.1 to 1551.5 cm.^{-1}), it seems safe to exclude the last five values of the table so that now seven possible values for $D(\text{CO})$ ranging from 11.054 to 6.738 volts, remain to be discussed. Nearly all of these values have at some time or other been proposed for $D(\text{CO})$ in the literature.

In order to come to a decision we try to use the other two predissociation limits at 11.538 and 9.558 volts. As the former is only an upper limit, its difference from the limit at 11.054, which is 0.484 volts, must be an upper limit to the difference of excitation energies of the products of dissociation at these two limits. The only differences of the excitation energies in the table which fulfil this condition are 0 or 0.15 or 0.31. The first would mean that the two predissociation limits, 11.054 and 11.538, lead to the same products of dissociation, i.e., the dissociation limits would be identical and nothing could be derived about the dissociation products. The second value would mean a dissociation into $^3P + ^1S$ at 11.054, and the third a dissociation into $^5S + ^3P$. As no decision between these three possibilities can be given, the predissociation limit at 11.538 does not lead to any selection of the seven proposed values for $D(\text{CO})$. It is compatible with any of them.¹⁵

In using the predissociation at 9.558 volts discovered by Gerö, in order to come to a selection, the three possibilities mentioned above have to be considered: (1) that there is a real predissociation in three succeeding levels leading to a definite dissociation limit, as assumed by Schmid and Gerö (36a); (2) that the intensity drops observed by Gerö are due to accidental predissociation; (3) that they are due to ordinary perturbations.

(1). If 9.558 is a real dissociation limit just as 11.054, the difference between the two, 1.496 volts, must be exactly equal to an energy difference

¹⁴ This conclusion would be wrong if the ground state would not dissociate into normal atoms. But there is no indication whatsoever for that.

¹⁵ Schmid and Gerö (36), as well as Brons (4), have assumed that the difference 0.484 of the two predissociation limits corresponds to the energy difference 0.544 of $^1D + ^1D$ and $^1S + ^3P$, and have thereby thought to confirm the value $D(\text{CO}) = 8.385$ volts. As, however, 0.484 is an upper limit for the energy difference this conclusion is not correct (cf. Herzberg (19a)).

of the two atoms, carbon and oxygen. In fact, the difference between $^3P + ^1S$ and $^1S + ^3P$ is 1.498, which is indeed a very close fit, well within the accuracy of the predissociation limits. From that it follows that at the upper predissociation limit (11.054 volts) a dissociation into $^3P + ^1S$ takes place, i.e., that $D(\text{CO})$ is 6.886 volts (cf. table 1). The closeness of the agreement between the difference of the predissociation limits and the difference of the excitation energies makes this value of $D(\text{CO})$ rather persuasive. But a similarly close fit was found by Brons for what he thought to be a predissociation at 9.66 volts, which later on was found to be only a perturbation.

(2). If the predissociation observed by Gerö is an accidental predissociation, and the fact that the drop of intensity occurs only for a few lines is strongly in favor of this assumption, then of course the only thing that can be said about the corresponding dissociation limit is that it must be lower than 9.558 volts. Consequently, the values $D(\text{CO}) = 11.054$ and 9.797 volts are excluded, whereas the remaining five values, 9.097 to 6.738, are all compatible with the predissociation at 9.558 volts. However, the two lowest values, 6.886 and 6.738, may be discarded here because assumption 2 is only needed instead of assumption 1 if as low a value for $D(\text{CO})$ is considered impossible from other considerations. Thus under assumption 2, we have the three possibilities $D(\text{CO}) = 9.097$ or 8.384 or 7.840 volts.

(3). If the drop in intensity observed by Gerö is due to ordinary perturbations, there would of course not be any predissociation at 9.558 volts and therefore all the seven possibilities for $D(\text{CO})$ previously mentioned, from 11.054 to 6.738 (cf. table 1), would still have to be considered. But assumption 3 will only be made if for some other reason values of $D(\text{CO}) \leq 9.558$ volts are excluded, so that this assumption really means that $D(\text{CO})$ is either 11.054 or 9.797 volts.

Thus only assumption 1 leads to a single unambiguous value for $D(\text{CO})$, namely, the very low value 6.886, whereas assumption 2 gives the three possibilities 9.097, 8.384, and 7.841 volts, and assumption 3 gives the two values 11.054 or 9.797 volts. To the author assumption 2 seems the most probable.

A Birge-Sponer extrapolation of the vibrational levels of the ground state and the $A^1\Pi$ state, for which a long series of vibrational levels is observed, does not lead to any definitive decision if account is taken of the uncertainty in these extrapolations. One may, perhaps, say that they seem rather incompatible with as low a value for $D(\text{CO})$ as 6.886 or 7.841 volts and also with as high a value as 11.054 volts.¹⁶

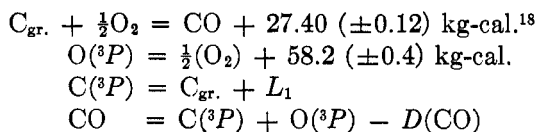
¹⁶ Birge and Hopfield (3) have found an apparent very rapid convergence of vibrational levels in the $F^1\Pi$ state, at about 104,500 cm^{-1} . This is difficult to reconcile

So far we have only discussed purely spectroscopic data, and we have seen that on the basis of these a completely unambiguous value for $D(\text{CO})$ cannot be given as yet. But at any rate it has been established that the true value for $D(\text{CO})$ must be one of the seven values given in the table. Of these from purely spectroscopic reasons 9.097 and 8.384 volts seem to be the most probable. Since these two values correspond to predissociation of the $B^1\Sigma$ state into $^3P + ^1D$ and $^1S + ^3P$, respectively, it follows from the Wigner-Witmer rules that the selection rule $\Delta S = 0$ is violated in the predissociation (singlet-triplet intercombination). This, however, is not an argument¹⁷ against these values, because the predissociation is weak, as mentioned above, and intercombinations are known to occur in carbon monoxide, though very weakly.

III. HEAT OF SUBLIMATION OF CARBON AND DISSOCIATION ENERGY OF THE CN RADICAL

One may try to come to an unambiguous value for $D(\text{CO})$ by using some non-spectroscopic data which, though perhaps not very accurate themselves, yet might help to decide between the possible $D(\text{CO})$ values enumerated above. By well-known thermochemical relations the value of $D(\text{CO})$ is closely connected with the value L_1 for the heat of sublimation of carbon and also with the heat of dissociation of the CN molecule.

From the equations:



it follows that

$$L_1 = D(\text{CO}) - 85.6 (\pm 0.5) \text{ kg-cal.}$$

It has to be noted that here L_1 means the heat of sublimation of graphite at 0°K. into normal carbon atoms in the 3P state, because $D(\text{CO})$ refers to dissociation into normal atoms from its lowest state.

with any of the $D(\text{CO})$ values discussed here. But, as pointed out in a private letter of Prof. Birge to the author, their data are not sufficient to establish definitely this convergence limit.

¹⁷ This argument is used by Asundi and Samuel (1).

¹⁸ Private communication from F. D. Rossini.

From the equations:

$$\begin{aligned}
 \text{CN} &= \text{C}({}^3P) + \text{N}({}^4S) - D(\text{CN}) \\
 \frac{1}{2}(\text{CN})_2 &= \text{CN} - 38.5 (\pm 2) \text{ kg-cal.} \quad (13) \\
 \text{C}({}^3P) + \text{O}({}^3P) &= \text{CO} + D(\text{CO}) \\
 \text{N}({}^4S) &= \frac{1}{2}(\text{N}_2) + 84.7 (\pm 0.1) \text{ kg-cal.} \\
 \frac{1}{2}\text{O}_2 &= \text{O}({}^3P) - 58.2 (\pm 0.4) \text{ kg-cal.} \\
 \text{CO}_2 + \frac{1}{2}\text{N}_2 &= \frac{1}{2}(\text{CN})_2 + \text{O}_2 - 128.2 (\pm 2.5) \text{ kg-cal.}^{19} \\
 \text{CO} + \frac{1}{2}\text{O}_2 &= \text{CO}_2 + 66.76 (\pm 0.03) \text{ kg-cal.}^{18}
 \end{aligned}$$

we obtain:

$$D(\text{CN}) = D(\text{CO}) - 73.4 (\pm 4) \text{ kg-cal.}$$

The values for L_1 and $D(\text{CN})$ which thus result from the various $D(\text{CO})$ values are given in the last three columns of table 1.

No definite conclusions can be drawn from the $D(\text{CN})$ values, because a direct determination of $D(\text{CN})$ has so far only been possible by Birge-Sponer extrapolations. These extrapolations do not agree with $D(\text{CN})$ values below about 6 volts, so that from this point of view the $D(\text{CO})$ values 11.054, 9.797, and 9.098 seem most probable.

The calculated values for L_1 range from 169 to 70 kg-cal. per mole. Until recently a value of about 150 kg-cal. derived by Kohn and Guckel was generally accepted. This would be compatible only with the $D(\text{CO})$ value 9.797 volts = 225.8 kg-cal. Now Marshall and Norton (27) propose a value $L = 178$ kg-cal., which as seen from table 1 would be only compatible with $D(\text{CO}) = 11.054$ volts. These two values 9.997 and 11.054, however, are according to the previous discussion very improbable from spectroscopic reasons, though they cannot be definitely excluded. They would only be possible if it were assumed that the predissociation at 9.558 volts found by Schmid and Gerö was in reality no predissociation.

The heat of sublimation of carbon, L , as determined by thermal methods corresponds to a sublimation into a mixture of atoms and diatomic molecules, whereas the value obtained from $D(\text{CO})$ corresponds to a sublimation into atoms only (L_1). The correction which has to be applied to the empirical value in order to get L_1 depends on $D(\text{C}_2)$, for which so far there is no reliable value. From the calculation of Vaughan and Kistiakowsky (38) it seems, however, impossible that this correction could bring Marshall and Norton's value down to 125 kg-cal. or even 75 kg-cal., as would be necessary if $D(\text{CO}) = 9.097$ or 6.886 volts, respectively.

Schmid and Gerö (36a), in order to explain the discrepancy between their value $D(\text{CO}) = 6.886$ volts and the experimental L value, have suggested

¹⁹ This is the average of the two rather diverging values given by K. v. Wartenberg and K. Schütza (39) and J. McMorris and R. M. Badger (28).

the following explanation. The products of the sublimation are not normal carbon atoms in the 3P state, but excited carbon atoms in the tetravalent 5S state. As the excitation energy of this state is 4.32 volts = 99 kg-cal., it would just explain the difference between the experimental $L = 178$ kg-cal. and the L_1 value calculated from $D(\text{CO}) = 6.886$ for sublimation into normal atoms: $L_1 = 73$ kg-cal. In equilibrium, of course, all atoms, even if they have left the solid carbon in the 5S state, would return to the 3P ground state and thereby give their energy back to the system, so that in equilibrium the low value $L_1 = 73$ kg-cal. ought to be measured. But in the experiments of Marshall and Norton the vapor pressure of carbon is determined not by equilibrium measurements but by the loss in weight of a piece of graphite in a vacuum at high temperatures. Thus once a carbon atom in the 5S state has left the graphite its excess energy over 3P will not be given back to the graphite, i.e., one has really to supply each carbon atom with the energy which is necessary to evaporate it in the 5S state. The value measured by Marshall and Norton would, according to this interpretation, be a sort of activation energy for evaporation of carbon, not the net sublimation energy.

A somewhat similar situation has very recently been found by Melville and Gray (29) for red phosphorus. The static vapor pressure is found to be about 10^7 times larger than the vapor pressure derived from the loss of weight of the solid in a vacuum. This is due to the fact that, as was shown by separate experiments, only P_2 molecules evaporate from and condense on solid red phosphorus, whereas, in equilibrium the vapor consists mostly of P_4 molecules, which of course have much lower energy than P_2 molecules. In equilibrium measurements it is the net energy difference, P_4 - solid, which matters, whereas for the dynamic method, it is the energy difference P_2 - solid. As the latter is much larger than the former, the anomalously low rate of evaporation results.

Though the assumption that carbon in the solid state (graphite, diamond) is in the 5S tetravalent state seems very probable, according to modern theories of valence, it is, however, not at all necessary to assume that immediately after evaporation a carbon atom is still in the 5S state.

As a first approximation we may expect on the basis of current valence theories that a 5S carbon atom is strongly attracted, whereas a 3P carbon atom is repulsed by solid carbon, so that we obtain the potential curves of figure 8, which intersect each other. In higher approximation, however, according to the Wigner-v. Neumann theorem of non-crossing of potential curves, the potential curves will follow the dotted lines which do not intersect. Thus in separating an atom from solid carbon it goes over into the normal 3P state, but only across a maximum of potential energy ("potential hill") which is higher than the asymptote. Nothing, so far, can be

said about the height of the potential hill. It might even be zero if a 3P atom instead of being repulsed is slightly attracted by solid carbon.

At any rate, these considerations show the following: (1) It is very improbable that if solid carbon is built up of 5S atoms the full excitation energy of the 5S state has to be supplied in excess of the net sublimation energy (L_1) in order to evaporate carbon in a vacuum. This means at the same time that Schmid and Gerö's low value, 6.886 volts, for $D(\text{CO})$ is very improbable. (2) It seems possible that the heat of sublimation of carbon measured in Marshall and Norton's way is larger than the net heat of sublimation in consequence of the potential hill. This opens a possibility that the heat of sublimation measured by Marshall and Norton is yet compatible with $D(\text{CO})$ values lower than 11.06 volts.

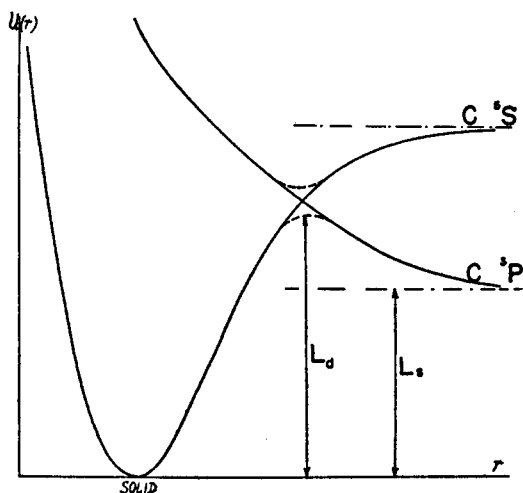


FIG. 8. Potential curves for sublimation of carbon

The two values for $D(\text{CO})$, 9.097 and 8.385 volts, which resulted as the most probable ones from a discussion of the purely spectroscopic data, are thus not necessarily in contradiction to the thermal data on L .²⁰ As it seems reasonable to assume the potential hill for evaporation of carbon as small as possible, the larger of the two $D(\text{CO})$ values given seems the more probable. Thus we have as the most probable values:²¹

²⁰ In the discussion following the paper at Pittsburgh it was pointed out by Dr. Dushman that the length of life of carbon filament lamps indicates that the vapor pressure is low and the heat of sublimation correspondingly high. But here again we have a dynamic method, which on the basis of the above argument should give too high a value for L .

²¹ Essentially the same values were also considered as most probable by Goldfinger, Lasareff, and Rosen (14) and Herzberg (19a). But they did not yet know the new data of Schmid and Gerö on the predissociation at 9.57 volts.

$$\begin{aligned}D(\text{CO}) &= 9.097 (\pm 0.005) \text{ volts} = 209.7 (\pm 0.1) \text{ kg-cal.}^{22} \\L_1 &= 124.1 (\pm 0.5) \text{ kg-cal.} \\D(\text{CN}) &= 5.9 (\pm 0.2) \text{ volts} = 136 (\pm 4) \text{ kg-cal.}\end{aligned}$$

But it has to be stressed that these values, though very probable, are not yet definitely established.

In concluding, a few ways may be mentioned which could lead to a definite decision.

A further investigation of the spectrum of the carbon monoxide molecule will be important in this connection, because it might result in the discovery of new predissociation limits and perhaps some which allow more definite conclusions to be drawn than the ones known so far.

Similarly, a further investigation of the spectrum of CN might result in a reliable determination of the dissociation energy of this molecule from which, according to the above, $D(\text{CO})$ can be obtained.

Furthermore, if it were possible to show definitely that the drop in intensity observed by Gerö in the fourth positive group of carbon monoxide is due to accidental predissociation or ordinary predissociation, it would mean that 9.57 volts is definitely an upper limit for $D(\text{CO})$, which in the above could only be assumed as very probable. This could comparatively easily be accomplished by investigating the fourth positive group of carbon monoxide in absorption with high dispersion. If there is no intensity anomaly in the 9-0 band at about 1300 A.U. in absorption, it means that the intensity drop observed in emission is really caused by predissociation.

A definite decision would also be possible if the question of the heat of sublimation of carbon could be unambiguously decided. In order to do that, a repetition of the early experiments of Kohn and Guckel, with modern methods, would be of great value, because it would supply an equilibrium value for L , from which a definite value for $D(\text{CO})$ can be obtained. In addition, the measurements of the equilibrium L could decide whether the proposed explanation for the high L value of the dynamic measurements of Marshall and Norton is correct. This of course could also be accomplished if the value of $D(\text{CO})$ and therewith of L_1 could be definitely established by spectroscopic means. Apart from its importance for the exact value of $D(\text{CO})$, L , and $D(\text{CN})$, the question of this potential hill for evaporation of carbon seems to have considerable interest in itself.

For an exact evaluation of the thermal equilibrium measurements a knowledge of the dissociation energy of C_2 is necessary; this might be expected from a further investigation of the C_2 spectrum.

In a recent paper which was received after the manuscript of this paper

²² The limits of error given do not include the possible error of the conversion factors.

was completed Goldfinger and Jeunehomme²³ have calculated the vapor pressure curves of carbon for the three values $L_1 = 168.8, 123.6,$ and 107.2 kg-cal., corresponding to the $D(\text{CO})$ values 11.06, 9.10, and 8.39 volts. The empirical vapor pressures, except the data obtained by the dynamical method, all lie between the curves for $L_1 = 168.8$ and 123.6 kg-cal. For $L_1 = 107.2$ kg-cal. the equilibrium vapor pressure would reach 1 atm. already at 2500°K. , which seems to contradict all experiments with carbon at such temperatures. The vapor pressures for $L_1 = 107.2$ kg-cal. are by several powers of 10 higher than any of those observed. Goldfinger and Jeunehomme therefore conclude that $L_1 = 123.6$ and correspondingly $D(\text{CO}) = 9.08$ volts are the most probable values for these quantities, i.e., essentially the same values as those proposed here.

SUMMARY

The various spectroscopic methods for the determination of dissociation energies D of diatomic molecules are briefly summarized. The conditions under which the D values obtained spectroscopically are dependable are treated in detail. On the basis of this discussion the various discordant values for $D(\text{CO})$ recently proposed by a number of investigators are dealt with. None of these values is without doubt. This must also be said about the heat of sublimation L of carbon and about $D(\text{CN})$ which may be obtained from $D(\text{CO})$ and well-known thermochemical data. However, a number of reasons are given which lead to $D(\text{CO}) = 9.097 (\pm 0.005)$ volts = $209.7 (\pm 1)$ kg-cal., $L_1 = 124$ kg-cal., $D(\text{CN}) = 5.9 (\pm 0.2)$ volts = $136 (\pm 4)$ kg-cal. as the most probable values. One of the points is that the predissociation of carbon monoxide recently found by Schmid and Gerö probably is a case of accidental predissociation. This eliminates the necessity of assuming as low a value for $D(\text{CO})$ as Schmid and Gerö have derived. The discrepancy between the value of L_1 given here and that recently obtained by Marshall and Norton from a measurement of the evaporation of carbon *in vacuo* is tentatively explained by the assumption of a potential hill which the individual atoms have to surmount in order to come from the solid to the evaporated state and *vice versa*. Investigations by which this question and the question of the values of $D(\text{CO})$, L , and $D(\text{CN})$ may be definitely settled are outlined.

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²³ The writer is indebted to Dr. Goldfinger for sending him an advance copy of this paper, which is now in press.

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Note added in proof: At the Princeton Symposium on Molecular Structure (December 31, 1936 to January 2, 1937) the question of the possibility of a potential hill for the evaporation of carbon was further discussed by K. F. Herzfeld, E. Teller, and the author. According to an idea of Teller a potential hill for the evaporation of graphite will arise owing to the fact that in the process of evaporation for every alternate carbon atom two C—C bonds have to be broken instead of the average 3/2 bonds, that is, on this assumption the dynamic heat of sublimation should be 33 per cent higher than the equilibrium value. This is, at least roughly, in agreement with the observed values if the equilibrium value for L given above is accepted. This agreement forms another argument in favor of the values for $D(\text{CO})$, L , and $D(\text{CN})$ proposed here.