

CarbonCarbon and CarbonHydrogen Bond Energies

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Taylor point out, as is well known to be the case for an immobile film (each particle of which occupies one site on a localized array)⁶ that this leads to a linear variation of heat of adsorption, q , with the fraction of the surface covered, θ . From the fact that Frankenburg's data does not follow such a law, they conclude that a theory of interactions on a surface in which all the sites involve the same energy of adsorption cannot account for the experimental results.

Their conclusion, in this respect, appears not to be well founded. Their rejection of interaction theories appears to be based primarily on the fact that the experimental results do not reproduce a linear variation of the heat of adsorption with the fraction of the surface covered. But this is not a characteristic of all possible types of adsorbed film, even for the kind of fixed interaction theory used in the case which they quote; such a linear variation is only to be expected on this theory for a random distribution, that is, an immobile film, of adsorbed particles, each of which occupies only one site on the surface. For mobile films⁶ and for all films, mobile or immobile, in which each adsorbed particle occupies more than one site⁷ on the array of the localized sites, the variation of the heat of adsorption may depart very much from a linear law in θ . Consequently, the experimental fact that a linear relation is not observed can provide no justification for rejecting out of hand an interaction theory.

Furthermore, it should be noted that the interaction theories to which reference has been made, and to one application of which Halsey and Taylor make appeal, assume that there is a fixed interaction energy between particles adsorbed on closest neighbor sites. It was pointed out by Roberts⁸ that for an actual surface this will not be so; that, in fact, the surface provides a two-dimensional periodic potential field, the local sites postulated by Langmuir⁹ being the potential minima of this field. It has been shown¹⁰ that when this periodic variation of the potential field* provided by the surface and the variation with distance of the interaction energy between two adsorbed particles are taken into account, neither a mobile nor an immobile film gives anything like a linear variation of the heat of adsorption with the fraction of the surface covered. As this physical model is a much closer representation of an actual surface than the fixed interaction model which was used in the earlier theoretical treatments of adsorption, it can be concluded that for an actual surface a linear variation of q with θ is scarcely to be expected in any case. This is entirely neglected by Halsey and Taylor, and it provides an additional reason for doubting the validity of the conclusion which they seek to deduce from the absence of a linear variation. There is not space in a letter to consider all the effects of the periodic potential field provided by an actual surface but a qualitative discussion has been given elsewhere.⁸ Miller and Roberts discussed theoretically a linear chain only, but by the use of other statistical methods it appears that the two-dimensional case can also be discussed and work is proceeding on this point.

Halsey and Taylor invoke the assumption that the energy difference between the lowest state in the gas phase and the lowest adsorbed state varies from site to site and that the interactions between adsorbed molecules can be neglected. It has been pointed out above that their argu-

ment depends on the neglect of a particular case of the fixed interaction theory and on the complete neglect of refinements of the theory which indicate that all adsorbed films give a variation of the heat of adsorption quite different from that which is the basis of their argument. Their rejection of theories which depend upon the interaction between adsorbed particles can scarcely be considered even to have been made plausible. Any effect which can be explained by the type of heterogeneity postulated by Halsey and Taylor is probably due to the fact that in the experiments which they discuss powdered metal is used and adsorbed gas on such a substratum forms a highly complex system.

¹ G. Halsey and H. S. Taylor, *J. Chem. Phys.* **15**, 624 (1947).

² W. G. Frankenburg, *J. Am. Chem. Soc.* **66**, 1827, 1838 (1944).

³ R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Teddington, England, 1939), Ch. X, p. 421.

⁴ For a precise definition of the terms mobile and immobile films and of localized arrays of sites in this connection see J. K. Roberts, *Some Problems in Adsorption* (Cambridge University Press, Teddington, England, 1939), p. 22; A. R. Miller, *Proc. Camb. Phil. Soc.* **43**, 232 (1947); A. R. Miller, *The Adsorption of Gases on Solids* (Cambridge University Press, Teddington, England, in press), Section 2.2.

⁵ J. K. Roberts, *Proc. Camb. Phil. Soc.* **34**, 399 (1938).

⁶ J. S. Wang, *Proc. Roy. Soc. A* **161**, 127 (1937), Fig. 1; A. R. Miller, *The Adsorption of Gases on Solids* (Cambridge University Press, Teddington, England, in press), Sections 2.4 and 2.5.

⁷ J. K. Roberts, *Proc. Camb. Phil. Soc.* **34**, 577 (1938), Fig. 4; A. R. Miller, *Proc. Camb. Phil. Soc.* **43**, 232 (1947), Figs. 2 and 5.

⁸ J. K. Roberts, *Some Problems in Adsorption* (Cambridge University Press, Teddington, England, 1939), Section 2.7.

⁹ I. Langmuir, *J. Am. Chem. Soc.* **40**, 1361 (1918).

¹⁰ A. R. Miller and J. K. Roberts, *Proc. Camb. Phil. Soc.* **37**, 82 (1941).

* Still assuming, however, that the adsorption energy of a particle adsorbed at one of these minima is the same for all the sites.

Carbon-Carbon and Carbon-Hydrogen Bond Energies

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June 14, 1948

WHEN the force constants ($k(\text{CC})$ and $k(\text{CH})$) for the aliphatic structures given in Table I are plotted as a function of internuclear distance ($R(\text{CC})$ and $R(\text{CH})$) as in Fig. 1, the well-known result is obtained that the larger force constants are found for the shorter bonds.¹ In order to obtain the corresponding carbon-carbon bond energies ($D(\text{CC})$) and the average carbon-hydrogen bond energies ($D(\text{CH})$), the atomic heats of formation (Q_a) of the molecules in Table I were calculated, using for the heat of sublimation of carbon $L(\text{C}) = 5.888 \text{ ev}^2$ or 7.334 ev^3 . For the $D(\text{CC}):R(\text{CC})$ curve only two points are known: $D(\text{C}_2(^3\Pi_u)) = 3.6 \text{ ev}$ from Herzberg⁴ and $D(\text{diamond}) = L/2 = 2.944 \text{ ev}$ based on $L(\text{C}) = 5.888 \text{ ev}$. For the $D(\text{CH}):R(\text{CH})$ curve two known points are $\bar{D}(\text{CH in CH}_4) = Q_a/4 = 3.88 \text{ ev}$ and $D(\text{CH}(^2\Pi_r)) = 3.47 \text{ ev}$ from Shidei.⁵ Skinner⁶ assumes a straight line relation for $D(\text{CH}):R(\text{CH})$. In the present calculations, however, the other points (C_2H_2 , C_2H_4 , C_2H_6) were found by dividing the corresponding Q_a values of these molecules in such a manner that both types of curve, $D(\text{CC}):R(\text{CC})$ and $D(\text{CH}):R(\text{CH})$ would have the same kind of curvature as the corresponding $k(\text{CC}):R(\text{CC})$ and $k(\text{CH}):R(\text{CH})$ curves. The procedure

TABLE I. Internuclear distances (R), force constants (k) and bond energies (D) of aliphatic carbon-carbon and carbon-hydrogen bonds.

Substance	$R(\text{CC})$ Å	$k(\text{CC})$ m.d./cm	$D(\text{CC})(\text{ev})$		$R(\text{CH})$ Å	$k(\text{CH})$ m.d./cm	$D(\text{CH})(\text{ev})$		$Q_a(\text{ev})$	
			$L=7.334$	$L=5.888^t$			$L=7.334$	$L=5.888$	$L=7.334$ (d)	$L=5.888^t$ (d)
1 C_2H_2	1.203 ^b	1.56 ^b	6.832	4.907	1.060 ^b	0.59 ^b	4.979	4.495	16.789	13.897
2 $\text{C}_2(^3\Pi_u)$	1.312 ^a	0.95 ^a	(5.54)	3.55 ^a	—	—	—	—	—	—
3 C_2H_4	1.353 ^b	0.82 ^b	5.125	3.349	1.076 ^b	0.53 ^b	4.467	4.188	22.993	20.101
4 Diamond	1.545 ^c	—	3.667	2.944	—	—	—	—	$L/2$	$L/2$
5 C_2H_6	1.569 ^b	0.45 ^b	3.535	2.922	1.098 ^b	0.48 ^b	4.212	3.834	28.807	25.925
6 CH_4	—	—	—	—	1.094 ^b	0.50 ^b	4.246	3.884	16.983	15.537
7 $\text{CH}(^2\Pi_r)$	—	—	—	—	1.120 ^a	0.43 ^a	(4.08)	3.47 ^a	—	—

^a G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939).

^b G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945).

^c R. W. G. Wyckoff, *The Structure of Crystals* (The Chemical Catalog Company, Inc., New York, 1931).

^d F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

^e G. Herzberg, *Phys. Rev.* **70**, 764 (1946).

^f H. D. Hagstrum, *Phys. Rev.* **72**, 947 (1947).

^g T. Shidei, *Jap. J. Phys.* **11**, 23 (1936).

is arbitrary, but as a matter of fact very little choice is possible. It is believed that the values given in Table I are very good estimates of these bond energies. The CH-bond energies are, of course, average values with the exception of $D(\text{CH}(^2\Pi_r))$.

If a similar calculation is now made based on $L=7.334$ ev, then it is seen that $D(\text{C}_2(^3\Pi_u)) \doteq 3.6$ ev and $D(\text{CH}(^2\Pi_r)) = 3.47$ ev no longer fit into the corresponding $D(\text{CC}):R(\text{CC})$ and $D(\text{CH}):R(\text{CH})$ curves, if curvatures like the $k(\text{CC}):R(\text{CC})$ and $k(\text{CH}):R(\text{CH})$ are to be maintained. In order to obtain proper energy-distance curves it is now necessary that $D(\text{C}_2(^3\Pi_u)) = 5.54$ ev and $D(\text{CH}(^2\Pi_r)) = 4.08$ ev. Obviously, these values do not check Herzberg⁴ and Shidei.⁵ It is conceivable that these investigators are wrong. However, several arguments will now be presented, indicating that the lower value of $L(\text{C}) = 5.888$ ev is more acceptable, in spite of the fact that the latest experimental determination of $L(\text{C})$ seems to indicate the higher value.⁶

1. The $D(\text{CC}):R(\text{CC})$ and $D(\text{CH}):R(\text{CH})$ curves based on $L(\text{C}) = 5.888$ ev have more nearly the curvature of the related $k(\text{CC}):R(\text{CC})$ and $k(\text{CH}):R(\text{CH})$ curves (Fig. 1).

2. A comparison of some molecular properties of the series of diatoms Be_2 , B_2 , C_2 , N_2 , O_2 , F_2 , Ne_2 shows that $D(\text{C}_2(^3\Pi_u)) = 3.55$ ev based on $L(\text{C}) = 5.888$ ev fits better than $D(\text{C}_2(^3\Pi_u)) = 5.54$ ev based on $L(\text{C}) = 7.334$ ev (Fig. 2).

TABLE II. Molecular properties of some first row elements.

State	R (Å)	ω_e (cm ⁻¹)	$x_e\omega_e$ (cm ⁻¹)	k m.d./cm	D (ev)
Be_2 $^1\Sigma_g^+$	$\sim \infty$	~ 0	~ 0	~ 0	~ 0
B_2 $^3\Sigma_g^-$	(1.76)	(891)	(8.0)	(0.24)	(1.2)
C_2 $^3\Pi_u$	1.312	1642	11.71	0.95	3.56 ^e
N_2 $^1\Sigma_g^+$	1.095	2360	14.45	2.29	9.76 ^d
O_2 $^3\Sigma_g^-$	1.208	1580	12.07	1.17	5.08
F_2 $^1\Sigma_g^+$	1.435 ^b	(790)	(8.0)	(0.34)	(~2.60)
Ne_2 $^1\Sigma_g^+$	$\sim \infty$	~ 0	~ 0	~ 0	~ 0

^a G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939).

^b M. T. Rogers, V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.* **63**, 2610 (1941).

^c G. Herzberg, *Phys. Rev.* **70**, 764 (1946).

^d A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (J. Wiley and Sons, Inc., New York, 1947).

3. The value of $\bar{D}(\text{CH in CH}_4) = 3.88$ ev fits better into the series of hydrides CH_4 , NH_3 , OH_2 , FH_3 .¹ The higher value of 4.25 ev would produce a $D(\text{CH}):R(\text{CH})$ curve for these hydrides of quite different curvature than the corresponding $k(\text{CH}):R(\text{CH})$ curve.

4. The lower value of $L(\text{C}) = 5.888$ ev fits appearance potential measurements.²

5. The removal energy of the first hydrogen atom from methane can be estimated from the curves of Fig. 1. The results based on $L(\text{C}) = 5.888$ ev agree well with other work,⁷⁻¹⁰ whereas similar calculations based on $L = 7.334$ ev do not correspond at all. Since the distances $R(\text{CH in CH}_4) = 1.094$ Å and $R(\text{CH}(^2\Pi_r)) = 1.121$ Å only differ by 0.027 Å, it was assumed that $R(\text{CH in CH}_3)$ and $R(\text{CH in CH}_2)$ are equally spaced between these values or $R(\text{CH in CH}_3) = 1.103$ Å and $R(\text{CH in CH}_2) = 1.112$ Å.

From a large plot of Fig. 1 the corresponding $\bar{D}(\text{CH})$ values can be found: $\bar{D}(\text{CH in CH}_3) = 3.736$ ev and $\bar{D}(\text{CH in CH}_2) = 3.47$ ev.

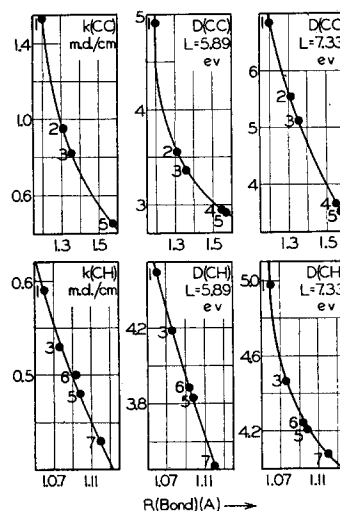


FIG. 1. Force constants (k ; m.d./cm), bond energies (D ; ev) of aliphatic carbon-carbon and carbon-hydrogen bonds as functions of internuclear distances (R ; Å). L = heat of sublimation of carbon = 5.89 or 7.33 ev; 1 = C_2H_2 ; 2 = $\text{C}_2(^3\Pi_u)$; 3 = C_2H_4 ; 4 = diamond; 5 = C_2H_6 ; 6 = CH_4 ; 7 = $\text{CH}(^2\Pi_r)$.

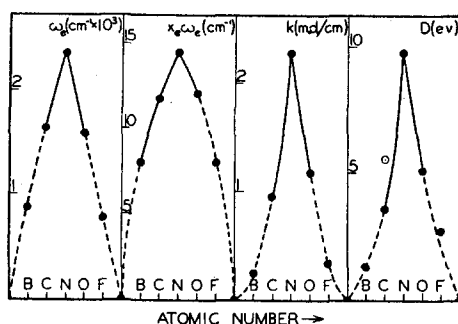
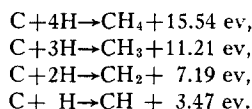
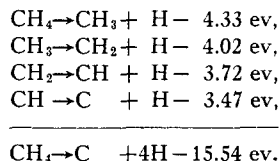


FIG. 2. Molecular constants of diatomic molecules
Be₂, B₂, C₂, N₂, O₂, F₂, Ne₂.

in CH₂) = 3.593 ev. Hence the Q_a values of this series are:



And the removal energies of the consecutive hydrogen atoms of methane are:



It is believed that these simple considerations lend weight to the lower value of the heat of dissociation $L(\text{C}) = 5.888 \text{ ev.}$

- ¹ For literature references see G. Glockler, *J. Chem. Phys.* **16**, 600 (1948).
- ² H. D. Hagstrum, *Phys. Rev.* **72**, 947 (1947).
- ³ L. Brewer, P. W. Gilles, and F. A. Jenkins, A.C.S. Meeting, Chicago, Illinois, April 19 (1948), Div. Phys. and Inorg. Chem., Paper No. 11.
- ⁴ G. Herzberg, *Phys. Rev.* **70**, 762 (1946).
- ⁵ T. Shidei, *Jap. J. Phys.* **11**, 23 (1936).
- ⁶ H. A. Skinner, *Trans. Faraday Soc.* **41**, 465 (1945).
- ⁷ K. Pitzer, *Chem. Rev.* **27**, 39 (1940).
- ⁸ G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.* **12**, 469 (1944).
- ⁹ D. P. Stevenson, *J. Chem. Phys.* **10**, 291 (1942).
- ¹⁰ H. H. Voge, *J. Chem. Phys.* **4**, 581 (1936).

Interpretation of X-Ray Scattering from Solutions of Long-Chain Electrolytes on the Basis of a Spherical Micelle

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June 28, 1948

X-RAY diffraction measurements on isotropic aqueous solutions of long-chain electrolytes have been interpreted largely on the basis of a lamellar micelle;¹ thus "spacings" calculated by the Bragg equation have been assigned to various identity periods in this structure. Hartley,² however, has long maintained that the micelle

must exist in spherical form. Recently a cylindrical model has been discussed by Harkins;³ this latter is, however, characterized by Bragg law "spacings." It is indicated below (1) that the observed x-ray diffraction patterns can arise from a system of spherical micelles and (2) that Bragg law "spacings" may be meaningless.

Unfortunately no diffraction measurements have as yet been reported in which the absolute intensity of the scattered radiation is known as a function of the scattering angle. The position of the rather broad diffraction peaks has been studied as a function of electrolyte concentration; some qualitative observations have been made on the variation of relative intensities of these peaks, or bands, with concentration.⁴

The highly simplified model considered here is one of spherical micelles of uniform radius, a_0 , whose short range order is characterized by a radial distribution function, $G(r)$. Ordinarily such distribution functions in liquid systems are calculated by means of the Fourier transform from diffraction data in which the absolute intensities of the scattered radiation are known as a function of the scattering angle.⁵ Since in the present case no such data are available the reverse process will be employed; namely, the angular variation in intensity of the scattered radiation will be calculated on the basis of an assumed radial dis-

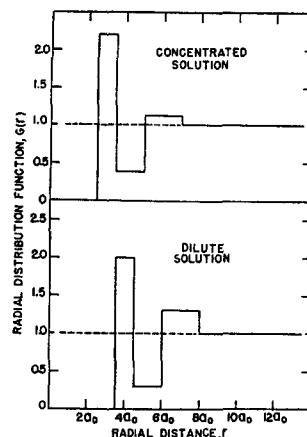


FIG. 1. Radial distribution functions for spherical micelles in concentrated and dilute solutions employed for the calculation of x-ray scattering. The radius of the micelle, a_0 , is taken as 16Å.

tribution function. All that can be expected from this treatment is qualitative agreement with respect to the form of the calculated and observed scattering curves. Under these conditions an extremely simple and highly approximate form of distribution function may be used.

Diffraction from two solutions of long-chain electrolyte, one dilute and the other concentrated, will be considered. The appropriate radial distribution functions employed are shown in Fig. 1 while the scattering curves calculated therefrom⁶ are plotted in Fig. 2. These calculations are based upon a micelle 16Å in radius and for Cu Kα radiation. The circles indicate those points for which the calculations were made.