

The Magnitude of the Experimental Error in the Adsorption of Nitrogen at 78°K on Various Surfaces

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room temperature, and consequently about 20° cooler than the bismuth mirror.

Our experiments thus prove that a volatile bismuth compound, presumably the trimethyl, is formed when dimethyl mercury is decomposed by atomic hydrogen in the vicinity of thin deposits of metallic bismuth. The fact that the mercury produced in the reaction was prevented from amalgamating with the mirror metal when the latter was slightly warmer than the reactor walls, provides strong evidence that the dimethyl mercury-hydrogen atom reaction was a gas phase process, and not merely a heterogeneous reaction on the surface of the bismuth deposit. The volatile bismuth compound must result, therefore, from direct reaction between alkyl radicals and the mirror. Full details of our technique and of correlative experiments now under way in this laboratory will be published elsewhere at a later date.

¹ G. Glockner and S. C. Lind, *The Electrochemistry of Gases and Other Dielectrics* (John Wiley & Sons, Inc., New York, 1939), p. 115.

² E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946).

³ F. Paneth and W. Hofeditz, Ber. **62B**, 1335 (1929); F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals* (Baltimore, 1935).

⁴ G. M. Harris and E. W. R. Steacie, J. Chem. Phys. **13**, 559 (1945).

Absorption by Hydrogen Sulfide in the 3.5μ-4.5μ Region*

EARL A. WILSON, JR. AND PAUL C. CROSS
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July 24, 1947

THE percent absorption by 90 cm of H₂S at 1-atmosphere pressure is plotted against wave number in Fig. 1. This spectrum was obtained with a fluorite prism

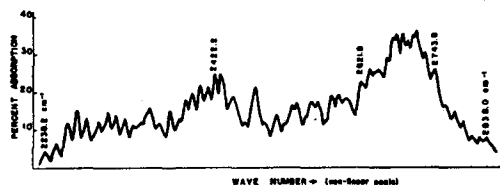


FIG. 1. Absorption by 90-cm. atm. of hydrogen sulfide in the 3.5μ-4.5μ region.

spectrometer which had a resolution of about 6 cm⁻¹ in this region.

Theoretically, it is possible for three vibrational transitions (ν_σ , ν_π , and $2\nu_\delta$) to contribute to this absorption. It is especially noteworthy that considerable absorption is observed in the region 2620 cm⁻¹–2450 cm⁻¹, where the P-branch of ν_σ may be expected to appear according to the calculations of Hainer and King,¹ but contrary to the reports of Nielsen and co-workers.²

A detailed tabulation of the absorption peaks at this resolution would be of little use unless accompanied by an analysis of the band envelope. A complete analysis will probably require new measurements at higher resolution.

* This work was performed under a contract between Brown University and the Office of Naval Research.

¹ R. M. Hainer and G. W. King, J. Chem. Phys. **15**, 89 (1947).

² H. H. Nielsen and E. F. Barker, Phys. Rev. **37**, 727 (1931); A. D. Sprague and H. H. Nielsen, J. Chem. Phys. **5**, 85 (1937); R. H. Nobel and H. H. Nielsen, Phys. Rev. **71**, 484 (1947).

The Magnitude of the Experimental Error in the Adsorption of Nitrogen at 78°K on Various Surfaces

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July 7, 1947

THE adsorption isotherms of nitrogen at -195°C have been widely used in recent years to determine the surface areas of solids. The published values for the surface areas have covered the range from about 2000 square meters per gram to about 0.1 square meter per gram. If the surface area is large, a small sample of about one gram is sufficient in the experimental procedure for the adsorption measurements. However, for materials of small surface areas, it is necessary to take large samples and, hence, use adsorption tubes with comparatively large dead spaces. It is the purpose of this note to ascertain that part of the experimental error which may result from the use of the various sized adsorption tubes which are necessary to accommodate adsorbents of widely varying surface areas.

Assuming the perfect gas laws to apply to the gas phase measurements, the following expression gives the number of moles, n , of gas adsorbed for a given initial point in an adsorption measurement.

$$n = p_i V_B / 300R - p_e V_B / 300R - p_e V_D / 78R, \quad (1)$$

where p_i = initial pressure of nitrogen introduced into the buret system.

p_e = equilibrium pressure of nitrogen after exposure to sample at 78°K.

V_B = volume of nitrogen (S.T.P.) in the buret system.

V_D = volume of nitrogen (S.T.P.) in the dead space of the adsorption tube.

R = gas constant (in appropriate units).

Room temperature is taken as 300°K and the temperature of the liquid nitrogen as 78°K.

If δn be the variation in the number of moles adsorbed, then the general expression for the percentage error is:

$$\frac{100\delta n}{n} = 100 \left[\frac{(V_B p_i + (V_B - 3.85 V_D) \delta p_e) + (p_i - p_e) \delta V_B + (3.85 p_e) \delta V_D}{V_B(p_i - p_e) - 3.85 p_e V_D} \right] \quad (2)$$

where δp_i , δp_e , δV_B , and δV_D are the corresponding variations in p_i , p_e , V_B , and V_D , respectively. It is to be noted,

TABLE I.

Sample (g)	B.E.T. Surface area (m ² /g)	V_D (ml)	δV_D (ml)	Pressures (mm Hg)		V_B (ml)	Percentage error $\frac{100\delta n}{n}$
				initial p_i	equi- librium p_e		
Cement*	21.5	1.5	15.3	0.15	104.0	39.2	1.1
Cotton*	31.1	0.7	121.	1.21	184.7	34.6	10.4
Bone char (1)	1.92	121.	7.0	0.07	582.	156.	0.20
Bone char (2)	1.92	121.	7.0	0.07	428.	0.4	0.27
Glass spheres	12.29	0.93	16.3	0.16	232.8	67.6	1.9
Activated coconut shell charcoal	0.71	1720.	5.7	0.06	392.7	0.3	0.12
Titanium oxide	1.08	9.9	4.1	0.04	131.4	78.9	2.1

* Data kindly furnished through the courtesy of R. L. Blane of this Bureau.

since variations may be positive or negative, that all the signs in the numerator of the above fraction are taken to be positive in order to obtain the maximum percentage error. The expression for the pressure drop, $p_i - p_e$, will always be positive.

An accuracy of ± 0.1 -mm Hg may be readily attained in the range of pressure measurements that are dealt with. Hence, δp_i and δp_e may each be set equal to 0.1. An accuracy of ± 0.1 milliliter in V_B may also be easily realized, since a calibration of the buret space with mercury is possible before the apparatus is assembled. Therefore, $\delta V_B = 0.1$. The dead space volume is generally determined by a calibration with helium. A reasonable value in the accuracy of such a measurement is 1 percent. The value for δV_D may be determined, consequently, by multiplying the value for V_D by 0.01.

The data contained in Table I were observed in a number of different adsorption tubes. These calculations were made for the first point of each isotherm. The calculation for subsequent points becomes more complicated, and the equation above is not directly applicable. It is obvious that the error in obtaining subsequent points is cumulative. Nevertheless, it is felt that the treatment above is indicative of the relative accuracy of this type of measurement.

It should be noted that the absolute accuracy of the surface determination includes other factors than those treated here. These other quantities are dependent on the validity of the assumptions in the B.E.T. theory and on the density of packing of the adsorbed nitrogen molecules. Since the dead space is obtained by a helium calibration, the above consideration shows that it is necessary to make this calibration with an accuracy adequate to the particular application.

The Formation of Per-Compounds in Relation to Electronegativities

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July 3, 1947

IT is pertinent to add to the letter of M. Haissinsky,¹ under the above title, the following remarks. They are largely taken from recent communications² in which we have surveyed some of the many factors that determine bond strengths.

It is clear that the electronegativity of the groups at either end of a bond is a very important factor in determining the strength of the bond. The bond strength commonly increases with the electronegativity of the bonded groups. Examples are numerous^{3,4} and the point has recently been stressed by Gordy⁵ who has given an empirical relation between bond strength and the product of the electronegativities of the groups concerned. It is equally clear, however, that the increase of bond strength with electronegativity of bonded groups can only be true up to a certain point: if the electronegativities are too great there will be insufficient electron density in the 'shared' region between the nuclei that is all important for bonding purposes. In other words, high bond strength

also requires adequate atomic orbital overlap, and too high an electronegativity of the bonded groups may result in reduced overlap. We therefore expect the rule of increasing bond strength with increasing electronegativity product to break down when we come to consider bonds between highly electronegative groups. Thus it is not surprising that Gordy's relation fails for the OO bond in H_2O_2 and probably for the FF bond.² As regards the OO bond the indications^{2,4} are that the strength *increases* with substitution of *less* electronegative groups for H. Similarly, the FF bond is *weaker* than the FCl bond, FF is weaker than FH, OO weaker than OH, and NN weaker than NH. If we accept the structure (I) advocated by Ingold and Ingold⁵ for N_2O_4 , the dissociation energy of the NN bond is 13 kcal./mole. The bond energy (E) must be distinguished from the dissociation energy^{2,6} but is likely also to be very low since the stretching force constant (k) is only 1.5×10^6 dyne/cm. In hydrazine,² however, $E(NN)$ appears to be ~ 64 kcal./mole, with $k(NN) = 3.6 \times 10^6$ dyne/cm. The great reduction of NN strength in N_2O_4 relative to N_2O can be explained as caused by reduced overlap in the NN bond of N_2O_4 consequent



upon the high dipole $\left(\begin{smallmatrix} \delta + & \delta - \\ NO_2 \end{smallmatrix} \right)$ in each NO_2 group. Glyoxal affords a similar example,² the CC bond strength appearing to be considerably weaker than considerations of the conjugation between its two C=O groups alone would indicate.

The conclusion of M. Haissinsky that elements whose electronegativities are smaller than a certain amount form per-compounds while those whose electronegativities are greater than this amount do not form per-compounds finds a natural explanation in terms of this factor of reduced atomic orbital overlap consequent upon too great an electronegativity. It is an important point of peroxide chemistry that the OO bond, to be strong, needs groups of low electronegativity attached to it.

¹ M. Haissinsky, J. Chem. Phys. 15, 152 (1947).

² Walsh, J. Chem. Soc., in press (2 papers).

³ W. Gordy, J. Chem. Phys. 14, 305 (1946).

⁴ Walsh, Trans. Faraday Soc. 42, 264 (1946).

⁵ Ingold and Ingold, Nature, 159, 743 (1947).

⁶ Walsh, Trans. Faraday Soc. 43, 60 (1947).

Addendum: A Relation between Bond Order and Covalent Bond Distance

[J. Chem. Phys. 15, 284 (1947)]

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THE paper, by G. N. Copley,¹ presenting the same model for obtaining multiple carbon bond distances as that which appeared in the appendix of this paper, has just come to my attention. Copley treats CC, CN, CO bonds and requires an empirical correction factor to his relation between bond order and bond distance.

¹ G. N. Copley, Chem. Ind. 663 (1941).