

## Pressure Dependence of Accommodation Coefficients

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## Pressure Dependence of Accommodation Coefficients

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The pressure dependence of accommodation coefficients of gases on metals has been explained by assuming that the accommodation coefficient varies linearly with the fraction of the surface covered with adsorbed gas. It is further assumed that the accommodation coefficient has a negligibly small value  $\alpha_0$  on a gas-free surface and an asymptotic value  $\alpha_\infty$  on a saturated surface. The assumptions lead to an accommodation coefficient isotherm which reproduces the pressure dependence of 119 accommodation coefficient values for ten gases on platinum with an average absolute deviation of 1.5 percent.

IT has long been recognized<sup>1-8</sup> that the accommodation coefficient of a gas on a metal surface depends upon the specific nature of the surface. Recently, values have been reported<sup>8</sup> for room temperature accommodation coefficients on platinum of ten gases over a wide range of pressure, so that sufficient experimental results are now available to test any theory which relates the value of the accommodation coefficient to characteristics of the surface which depend upon the gas pressure. It is the purpose of this paper to show that the observed variation of the accommodation coefficients with pressure can be explained quantitatively by considering the effect of adsorption on the metal surface. Although it frequently has been suggested<sup>1-8</sup> that adsorption is responsible for the increase in the value of the accommodation coefficient in changing from a gas-free to a gas-covered surface, no general functional relation has been proposed to date.

If we assume that the accommodation coefficient varies linearly with the fraction of the surface covered, the following relation holds:

$$\alpha = (1 - \Theta)\alpha_0 + \Theta\alpha_\infty, \quad (1)$$

<sup>1</sup> (a) J. K. Roberts, Proc. Roy. Soc. **A129**, 146 (1930); (b) **A135**, 192 (1932); (c) **A142**, 519 (1933).

<sup>2</sup> W. B. Mann, Proc. Roy. Soc. **A146**, 776 (1934).

<sup>3</sup> W. B. Mann and W. C. Newell, Proc. Roy. Soc. **A158**, 397 (1937).

<sup>4</sup> (a) W. C. Michels, Phys. Rev. **40**, 472 (1932); (b) **52**, 1067 (1937).

<sup>5</sup> B. Raines, Phys. Rev. **56**, 691 (1939).

<sup>6</sup> P. Rolf, Phys. Rev. **65**, 185 (1944).

<sup>7</sup> L. B. Thomas and F. Olmer, J. Am. Chem. Soc. **65**, 1036 (1943).

<sup>8</sup> I. Amdur, M. M. Jones, and H. Pearlman, J. Chem. Phys. **12**, 159 (1944).

where  $\alpha_0$ ,  $\alpha$ , and  $\alpha_\infty$  are the accommodation coefficients at zero pressure, at the pressure at which the fraction  $\Theta$  of the surface is covered, and at infinite pressure, respectively. Since we are dealing with gases adsorbed on relatively plane metallic surfaces at very low pressures and at temperatures far above the critical, we shall assume that the fraction of the surface covered is given by the simple Langmuir relation

$$\Theta = bp/(1 + bp), \quad (2)$$

where  $p$  is the gas pressure and  $b$  is a constant for a given gas and depends only upon the temperature. Equations (1) and (2) may be combined to give the following relation for the pressure dependence of the accommodation coefficient:

$$\alpha = \alpha_0 + \frac{bp}{1 + bp}(\alpha_\infty - \alpha_0) = \frac{1}{1 + bp}\alpha_0 + \frac{bp}{1 + bp}\alpha_\infty. \quad (3)$$

It will be assumed, for the present, that the magnitude of  $\alpha_0$  is sufficiently small so that it may be neglected in Eq. (3). This assumption is in accord with the available room temperature information shown in Table I which compares  $\alpha_0$  and  $\alpha_\infty$  for several gases and metals. Although the

TABLE I. Comparison of room temperature values of  $\alpha_0$  and  $\alpha_\infty$ .

Gas	Metal	$\alpha_0$	$\alpha_\infty$
Helium <sup>a</sup>	Platinum	0.03	0.403
Helium <sup>b</sup>	Platinum	0.07	0.403
Helium <sup>c</sup>	Nickel	0.07	0.403
Helium <sup>d</sup>	Tungsten	0.04	0.403
Neon <sup>d</sup>	Tungsten	0.05	0.700

<sup>a</sup> See reference 2 of text.

<sup>b</sup> See reference 6 of text.

<sup>c</sup> See reference 5 of text.

<sup>d</sup> See reference 4b of text.

TABLE II. Test of general relation  $\alpha = [bp/(1+bp)]\alpha_\infty$ .

Gas	$\alpha_\infty$	$b$ (mm <sup>-1</sup> )	$P$ (mm)	$\alpha_{\text{obs}}$	$\alpha_{\text{calc}}$	$100 \frac{ \Delta\alpha }{\alpha_{\text{obs}}}$	Gas	$\alpha_\infty$	$b$ (mm <sup>-1</sup> )	$P$ (mm)	$\alpha_{\text{obs}}$	$\alpha_{\text{calc}}$	$100 \frac{ \Delta\alpha }{\alpha_{\text{obs}}}$					
He	0.409	276	0.009639	0.300*	0.298	0.7	Xe	0.881	206	0.007116	0.469*	0.522	11.3					
				0.01011	0.296	1.7					0.01127	0.736*	0.614	16.6				
				0.04097	0.386	2.6					0.03784	0.794	0.779	1.9				
				0.05250	0.376	1.9					0.06307	0.810	0.816	0.7				
				0.06076	0.392	1.5					0.07540	0.848	0.826	2.6				
				0.07714	0.391	0.0					0.1250	0.865	0.846	2.2				
				0.09940	0.385	2.6					0.1725	0.869	0.854	1.7				
				0.1127	0.398	0.3					0.2111	0.866	0.859	0.8				
				0.1450	0.400	0.0					0.2524	0.849	0.862	1.5				
				0.1740	0.398	0.8					0.2891	0.856	0.864	0.9				
				0.1995	0.406	1.0					0.3352	0.835	0.866	3.7				
				0.2210	0.394	2.3					0.3986	0.864	0.868	0.5				
				0.2461	0.411	1.7									Mean 3.7			
				0.2596	0.408	1.0					H <sub>2</sub>	0.316	545	0.008717	0.253*	0.261	3.2	
				0.2854	0.403	0.2									0.009725	0.270*	0.266	1.5
				0.3223	0.404	0.2									0.04916	0.309	0.304	1.6
				0.3417	0.400	1.2									0.1013	0.311	0.310	0.3
				0.3583	0.406	0.2									0.1027	0.316	0.310	1.9
				Mean 1.1											0.1536	0.316	0.312	1.3
Ne	0.718	165	0.01104	0.466	0.462	0.9	0.2039	0.312	0.313	0.3								
				0.01374	0.487	1.8	0.2479	0.309	0.313	1.3								
				0.04714	0.642	1.2	0.3111	0.309	0.314	1.6								
				0.06002	0.659	1.4	0.3434	0.308	0.314	1.9								
				0.1018	0.685	1.5					Mean 1.5							
				0.1709	0.700	1.3	D <sub>2</sub>	0.396	697	0.01162	0.350*	0.353	0.9					
				0.2322	0.705	1.1					0.04888	0.388	0.385	0.8				
				0.2900	0.706	0.7					0.06222	0.386	0.387	0.3				
				0.3669	0.700	0.4					0.1041	0.395	0.391	1.0				
				0.3940	0.703	0.1					0.1056	0.392	0.391	0.3				
				0.4671	0.691	2.2					0.1439	0.394	0.392	0.5				
				Mean 1.1							0.1767	0.398	0.393	1.3				
A	0.870	195	0.01095	0.596*	0.596	0.0					0.2048	0.399	0.393	1.5				
				0.01312	0.612	2.5					0.2112	0.396	0.393	0.8				
				0.05125	0.807	1.7					0.2903	0.389	0.394	1.3				
				0.1045	0.833	0.2					0.3470	0.389	0.394	1.3				
				0.1589	0.851	0.8					0.3804	0.387	0.395	2.1				
				0.1643	0.847	0.2	0.4148	0.385	0.395	2.6								
				0.2157	0.848	0.5					Mean 1.1							
				0.2252	0.856	0.5	N <sub>2</sub>	0.783	392	0.009121	0.620*	0.612	1.3					
				0.3015	0.853	0.5					0.01146	0.625	0.641	2.6				
				0.3497	0.845	1.7					0.04950	0.758	0.745	1.7				
				0.3883	0.842	2.1					0.09147	0.765	0.762	0.4				
				Mean 1.0							0.1008	0.761	0.764	0.4				
Kr	0.878	126	0.009823	0.445*	0.487	9.4					0.1106	0.761	0.765	0.5				
				0.04863	0.776	2.7					0.1524	0.784	0.770	1.8				
				0.06158	0.800	2.5					0.2107	0.776	0.774	0.3				
				0.1040	0.826	1.0					0.2181	0.775	0.774	0.1				
				0.1077	0.842	2.6					0.2973	0.767	0.777	1.3				
				0.1451	0.850	1.6					0.3255	0.763	0.777	1.8				
				0.1818	0.857	1.5									Mean 1.1			
				0.2173	0.855	0.6	CO	0.778	702	0.008454	0.665*	0.666	0.2					
				0.2451	0.843	1.7					0.05471	0.756	0.758	0.3				
				0.2914	0.841	2.0					0.09192	0.768	0.766	0.3				
				0.3484	0.841	2.4					0.1216	0.778	0.769	1.2				
				0.3764	0.840	2.7					0.1778	0.776	0.772	0.5				
				0.4165	0.840	2.9					0.2064	0.781	0.772	1.2				
				0.4766	0.826	5.0					0.2509	0.765	0.774	1.2				
				Mean 2.8							0.3017	0.768	0.774	0.8				
											0.3311	0.767	0.775	1.0				
												Mean 0.7						

TABLE II.—Continued.

Gas	$\alpha_\infty$	$b$ (mm <sup>-1</sup> )	$P$ (mm)	$\alpha_{obs}$	$\alpha_{calc}$	$100 \frac{ \Delta\alpha }{\alpha_{obs}}$
O <sub>2</sub>	0.800	242	0.008557	0.534*	0.541	1.3
			0.05029	0.742	0.741	0.1
			0.09046	0.787	0.767	2.5
			0.1226	0.782	0.775	0.9
			0.1520	0.784	0.781	0.4
			0.2080	0.792	0.786	0.8
			0.2306	0.779	0.787	1.0
			0.2579	0.782	0.789	1.3
			0.3054	0.770	0.791	2.7
			0.3259	0.777	0.792	1.9
			Mean 1.3			

$\alpha_\infty$  values are taken from measurements using a platinum wire,<sup>8</sup> they are assumed to be essentially independent of the wire used because of the saturation of the metal surface.

Inspection of Eq. (3) shows that the elimination of  $\alpha_0$  produces an extremely small effect on values of  $\alpha$  calculated at pressures where an appreciable fraction of the surface is covered, since the small  $\alpha_0$  term is, under these conditions, multiplied by the term  $1/(1+bp)$  which approaches zero as the surface approaches saturation. The simplified theoretical equation for the pressure variation of the accommodation coefficient will therefore be taken as

$$\alpha = \frac{bp}{1+bp} \alpha_\infty \quad (4)$$

or

$$1/\alpha = 1/\alpha_\infty + 1/(bp\alpha_\infty). \quad (5)$$

Values of  $b$  and  $\alpha_\infty$  were computed from Eq. (5) for each gas listed in Table II from the observed accommodation coefficients at the tabulated pressures. The method of least squares was used with the standard weighting procedure<sup>9</sup> necessitated by the inversion of Eq. (4) to produce Eq. (5) which is linear in the reciprocals of the desired constants. The starred  $\alpha_{obs}$  values differ from those originally published<sup>8</sup> because of a correction required in the original meter readings from which these values were computed. These readings fell on a different scale than the others and were found, upon calibration of the meter, to be in error by about 1 percent. This relatively

small error has a large effect on the accommodation coefficients at the low pressures involved because of the small difference between the meter reading in vacuum and at the given pressure. The entries under  $\alpha_{calc}$  were computed from Eq. (4) using the  $b$  and  $\alpha_\infty$  values given in the table.

The agreement between the observed and calculated accommodation coefficients, as expressed by the absolute percentage deviations, seems quite satisfactory in all but three cases, the first value for krypton and the first two values for xenon. This may be caused by the difficulty of obtaining precise values of  $\alpha_{obs}$  in these cases, where the low pressure and the low free molecule conductivity combine to give a very small difference between the energies required to heat the platinum wire to a given temperature in vacuum and in the gases at the recorded pressures. It is also possible, but less likely, in the opinion of the author, that these larger deviations result from the assumption that  $\alpha_0$  is negligible in comparison with  $\alpha_\infty$  since, in this case, it would be difficult to explain the opposite sign of the deviations in the first two entries for xenon.

It is not possible to make a quantitative comparison between the results of Table II and those of other investigators who have determined accommodation coefficients on platinum, since

TABLE III.

Investigator	Gas	$\alpha_{obs}$	$P_{obs}$ (mm)	$P_{calc}$ (mm)
Rolf	He	0.170	$1 \times 10^{-3}$ to $1 \times 10^{-2}$	$2.6 \times 10^{-3}$
Thomas and Olmer	H <sub>2</sub>	0.220	0 to $5 \times 10^{-2}$	$5.0 \times 10^{-3}$
Thomas and Olmer	D <sub>2</sub>	0.295	0 to $5 \times 10^{-2}$	$4.2 \times 10^{-3}$
Thomas and Olmer	He	0.238	0 to $5 \times 10^{-2}$	$4.2 \times 10^{-3}$
Thomas and Olmer	Ne	0.57	0 to $5 \times 10^{-2}$	$2.4 \times 10^{-2}$
Thomas and Olmer	A	0.89	0 to $5 \times 10^{-2}$	
Thomas and Olmer	O <sub>2</sub>	0.74	0 to $5 \times 10^{-2}$	$4.9 \times 10^{-2}$

only Rolf<sup>6</sup> and Thomas and Olmer<sup>7</sup> have published details which show that the heat flow problem has been properly analyzed, and in both cases only single values of the accommodation coefficient are reported for a wide range of pressure. Furthermore, the results of Thomas and Olmer, particularly those near unity, are uncertain because of an error in one of their formulas.<sup>8</sup> In Table III the accommodation coefficients reported by Rolf and by Thomas and

<sup>9</sup> J. B. Scarborough, *Numerical Mathematical Analysis* (The Johns Hopkins Press, Baltimore, 1930), p. 370ff.

Olmer have been combined with the constants of Table II to ascertain if the pressures calculated from Eq. (4) fell within the ranges cited by these authors.

The author feels that the qualitative agree-

ment in six of the seven cases in Table III tends to support the present simple adsorption theory but that more reliable confirmation must await additional experimental results of the type given in Table II.

## Theory of the Non-Tetrahedral Carbon Atom

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(Received March 18, 1946)

The hybridization of  $s$  and  $p$  orbitals to give non-tetrahedral orbitals is discussed. The results are applied to cyclic hydrocarbons. For cyclopentane the theory yields an H-C-H angle of  $111^\circ 1'$ , and for cyclobutane an H-C-H angle of  $180^\circ$ .

THE method of directed valence bonds as developed by Pauling<sup>1</sup> is based on the following postulates. A single bond arises from the interaction of two unpaired electrons of opposite spin derived from different atoms. Of two orbitals in an atom the one which can overlap more with the orbital of another atom will form the stronger bond with that atom. The direction of this bond will be that direction in which the orbital wave functions of the two atoms overlap as much as possible. In applying these postulates to the carbon atom Pauling assumed that orbitals were formed from a combination or hybridization of  $s$  and  $p$  orbitals. The hybridization was made in such a way as to yield the maximum bond strengths.

### HYBRIDIZATION IN THE NON-TETRAHEDRAL CARBON ATOM

Let us now consider how this theory is to be altered if we specify one of the valence angles of the carbon atom. Such a restriction is present in compounds such as cyclopropane, cyclobutane, and cyclopentane. It will be assumed that a certain amount of symmetry exists. Thus numbering the bonds of carbon as 1, 2, 3, and 4, it will be assumed that bonds 1 and 2 are equivalent and that bonds 3 and 4 are equivalent.

<sup>1</sup>L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931). See also W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927); J. C. Slater, Phys. Rev. **37**, 481 (1931).

It is assumed that the radial parts of the wave functions  $\psi_s, \psi_{px}, \psi_{py}, \psi_{pz}$  are so similar that their differences are negligible. The angular parts, normalized to  $4\pi$ , are given by the equations

$$s = 1, \quad (1)$$

$$p_x = \sqrt{3} \sin \vartheta \cos \varphi, \quad (2)$$

$$p_y = \sqrt{3} \sin \vartheta \sin \varphi, \quad (3)$$

$$p_z = \sqrt{3} \cos \vartheta, \quad (4)$$

where  $\vartheta$  and  $\varphi$  are the angles used in polar coordinates.

The angular part of each of the bond-forming eigenfunctions is approximated by functions of the form

$$f_i = a_i s + b_i p_x + c_i p_y + d_i p_z, \quad (5)$$

where  $i$  is 1, 2, 3, or 4. The coefficients  $a_i, b_i, c_i$ , and  $d_i$  are determined by the normalization condition

$$a_i^2 + b_i^2 + c_i^2 + d_i^2 = 1, \quad (6)$$

and by the orthogonality condition

$$a_i a_j + b_i b_j + c_i c_j + d_i d_j = 0, \quad i \neq j. \quad (7)$$

The direction of the maximum of the first bond eigenfunction is arbitrary. It is chosen to lie along the  $x$  axis. Hence

$$f_1 = a_1 s + (1 - a_1^2)^{1/2} p_x, \quad (8)$$

where  $b_1$  has been replaced by  $(1 - a_1^2)^{1/2}$  so that Eq. (6) might be satisfied.