295. *Binding Energies in Hydrocarbons.*

By T. L. Cottrell.

The energy of a molecule at ordinary temperatures may be regarded as being composed of its chemical binding energy, its zero-point vibrational energy, and its heat content relative to the molecule at 0° K. The last two quantities have been subtracted from the total energy of several typical hydrocarbons, to give an estimate of the total binding energy. This has been split into " binding-energy terms " per bond, and it is found that the replacement of conventional bond-energy terms by " binding-energy terms " has little effect on discussions involving them. In particular, estimates of resonance energy and steric strain are almost unchanged. It is noteworthy that the binding energy of *cyclo*hexane is less than that calculated on the basis of " binding-energy terms "; it is shown that this indication of the relative instability of *cyclo*hexane, which is not indicated by conventional bond-energy terms, is in agreement with other evidence.

It is well known that conventional bond-energy terms include the vibrational, rotational, and translational energies of the molecule, as well as the chemical binding energy. Pauling (" The Nature of the Chemical Bond," New York, 1940, p. 54) has stated that there is no " appreciable disadvantage " in this, and Mulliken, Reike, and Brown (*J. Amer. Chem. Soc.*, 1941, **63**, 41) have expressed the opinion that errors introduced into calculation of conjugation energies by omitting to correct ΔH values for thermal energy and zero-point vibrational energy probably cancel, but suggested that it would be desirable to verify this. On the other hand, the importance of the zero-point vibrational energy correction was pointed out by Zahn as early as **1934** (*J. Chem. Physics*, **2**, 671), but at that time insufficient experimental evidence was available for a satisfactory discussion of the effect. It has also been suggested that non-additivity of bond-energies in the paraffins (cf. Rossini, *Chem. Reviews*, 1940, **27**, 1) is partly due to differences in the zero-point energies of isomers (Deitz, *J. Chem. Physics*, 1935, **3**, 58; Wolkenstein, *Compt. rend.* (*Doklady*) *Acad. Sci. U.R.S.S.*, 1946, **51**, 213). Again, it has been suggested by Dewar (*Trans. Faraday Soc.*, 1946, **42**, 767) that the discrepancy between the resonance energy of benzene, as obtained from heat of hydrogenation data and from comparison of the heat of formation calculated on the basis of bond energies with that observed from combustion data, results from a systematic difference between the internal kinetic energy of open-chain and cyclic compounds. It has been shown (Cottrell and Sutton, *J. Chem. Physics*, 1947, **15**, 685; cf. also Wheland, "The Theory of Resonance," New York, 1944, Ch. 3) that the discrepancy discussed by Dewar is not, in fact, due to the causes he mentions, but it certainly seems true that there is likely to be some difference in internal kinetic energy between open-chain and cyclic compounds, and also between isomers in the same series.

Zahn (*loc. cit.*) and Dewar (*loc. cit.*) have both argued that there are no theoretical reasons for expecting internal kinetic energy to be an additive bond property. This is not altogether true. Vibrations which involve the relative motions of one light atom and one heavier one, typically C–H vibrations, are fairly independent of the vibrations of the rest of the molecule. Hydrogen frequencies contribute largely to the zero-point energy, and it might therefore be expected that that quantity would depend roughly on the number of C–H bonds present, and thus be, in hydrocarbons at least, very approximately, an additive bond property. The heat content, on the other hand, being concerned with translational and rotational motion as well as vibrational, and its vibrational component being chiefly dependent on the low-frequency skeletal vibrations, is not likely to be an additive property of the bonds, but to depend on the shape of the molecule. It should be remembered that the zero-point energy is about ten times as great as the heat content.

Many data have recently been obtained on the thermodynamic properties of hydrocarbons by workers on the American Petroleum Institute Research Project No. 44 (" Tables of Selected Properties of Hydrocarbons "), and it seemed of interest to make use of them in an examination of the effect of internal kinetic energy on the additivity of bond energies, resonance, and steric strain.

Data used.—All data refer to the compounds in the ideal gas state. Heats of formation from the elements in their standard states at 298·1° K. and 0° K., and values of the heat content $H^0_{298\cdot1} - H^0_0$, have been taken from A.P.I. 44 data (*op. cit.*) for all the compounds considered with the exception of *cyclo*propane and *cyclo*butane, which are not covered by that investigation. The heat of formation of *cyclo*propane is from Rossini (" The Chemical Background to Engine Research ", 1943, Ch. 2, quoted by Skinner, *Trans. Faraday Soc.*, 1945, **41**, 645), and its thermodynamic properties have been calculated from spectroscopic data by Linnett (*J. Chem. Physics*, 1938, **6**, 692) and by Kistiakowsky and Rice (*ibid.*, 1940, **8**, 610), using the molecular dimensions given by Pauling and Brockway's electron-diffraction study (*J. Amer. Chem. Soc.*, 1937, **59**, 1223). The third law entropy has been shown by Ruehrwein and Powell (*ibid.*, 1946, **68**, 1066) to agree with that calculated from molecular data. Since this work, a new electron-diffraction study of *cyclo*propane has been made by Bastiansen and Hassel (*Tids. Kjemi Berg.*, 1946, **6**, 71), giving slightly altered molecular dimensions. The thermodynamic properties have therefore been recalculated, using the new values for the molecular dimensions, and the frequency assignment, which is that used by Kistiakowsky and Rice (*loc. cit.*) as modified by Smith (*Physical Rev.*, 1941, **59**, 924), quoted by Herzberg (" Infra Red and Raman Spectra of Polyatomic Molecules ", New York, 1945, p. 352). These changes make little difference to the results, which at 298·16° K. are: $S = 56{\cdot}85$ e. u., $H^0 - H^0_0 = 2740$ cals., $C_p = 13{\cdot}48$ cals./deg. Ruehrwein and Powell (*loc. cit.*) give 56·75 for the calorimetric entropy at 298·16° K.; these values for the thermodynamic functions therefore appear to be reliable. No sufficiently accurate determination of the heat of formation of *cyclo*butane is available; its thermodynamic properties have been calculated from molecular data (Cottrell, *Trans. Faraday Soc.*, in the press).

The zero-point energies have been obtained on the harmonic oscillator approximation, *i.e.*, Zpt. $E = \frac{1}{2}\sum_i \boldsymbol{h}\nu_i = 0{\cdot}001429\ \Sigma\nu_1(\text{cm.}^{-1})$ kcals./mole. An estimate of the magnitude of the effect of anharmonicity may be obtained by considering the zero-point energy of water. The fundamental frequencies of the H_2O molecule as quoted by Herzberg (*op. cit.*, p. 281) are 1595·0, 3651·7, and 3755·8 (cm.$^{-1}$), giving a zero-point energy of 12·86 kcals./mole. Darling and Dennison (quoted by Herzberg, *op. cit.*) have obtained the anharmonic constants, and the true zero-point energy estimated by these authors is $4631{\cdot}2_5$ cm.$^{-1}$ or 13·24 kcals./mole. The error due to neglect of anharmonicity is thus about 3%. Though the absolute values of zero-point energies may be out by this amount, the figures are probably quite useful for comparative purposes, since it seems reasonable to assume that *differences* in anharmonicities in molecules containing the same type of bonds will be much less than this.

A pleasing confirmation of the view that *differences* in errors in zero-point energies are very small comes from the work of Ingold and his collaborators on the spectra of benzene and its deuterated derivatives (cf. Ingold, Septième Conseil de Chimie Solvay, " Isotopes in the Spectroscopy of Polyatomic Molecules with Special Reference to the Benzene Molecule "). Consideration of the isotope effect on the position of the electronic origin of the transition $A_{1g} \rightarrow B_{2u}$ for benzene and hexadeuterobenzene shows that the electronic origin of hexadeuterobenzene lies 200 cm.$^{-1}$ further out towards the far ultra-violet than that of benzene. The energy of an electronic transition is not simply the difference between the electronic energies of the states concerned; it is this plus the difference in zero-point energies. The electronic energy is, to a high degree of approximation, unaltered by isotopic substitution; the difference between the electronic origins must therefore be due to differences in zero-point energies. For benzene and hexadeuterobenzene complete sets of vibration frequencies have been given for both electronic states, and the zero-point energies calculated on the harmonic oscillator approximation. The calculated isotopic shift of the electronic origin is 208 cm.$^{-1}$, in very good agreement with the observed shift of 200 cm.$^{-1}$. This agreement, is, however, rather better than might be expected, considering the errors to which some of the frequencies are liable.

The vibrational frequencies used to obtain the zero-point energies have been taken from the assignments quoted by Herzberg (*op. cit.*) except as discussed below. For propane, for which Herzberg does not quote a complete assignment, that due to Pitzer (*J. Chem. Physics*, 1944, **12**, 310) was used. For *n*-butane, *n*-pentane, and *n*-hexane the frequencies have been estimated according to Pitzer (*Ind. Eng. Chem.*, 1944, **36**, 829; *J. Chem. Physics*, 1940, **8**, 711). The frequencies for *iso*butane and *neo*pentane are from Pitzer and Kilpatrick (*Chem. Reviews*, 1946, **39**, 435). It is of interest to compare them with those given by Wolkenstein (*loc. cit.*). The sums of the frequencies, not including those due to torsional oscillation, as obtained from the results of the American and Russian workers are given below, to the nearest 100 wave-numbers.

	Pitzer.	Wolkenstein.		Pitzer.	Wolkenstein.
n-Butane	55,800	55,400	*n*-Pentane	68,000	67,400
*iso*Butane	55,500	54,900	*neo*Pentane	66,800	67,000

The agreement is reasonably good, but the difference is sufficiently great to render doubtful the significance of the last two figures to which Wolkenstein quotes zero-point energies. We have added an arbitrary 200 wave-numbers for each torsional oscillation. The assignment for 2 : 2-dimethylbutane is due to Kilpatrick and Pitzer (*J. Amer. Chem. Soc.*, 1946, **68**, 1070). For ethylene, propylene, *cis*-but-2-ene, *trans*-but-2-ene, and *iso*butene, the assignments are due to Kilpatrick and Pitzer (*J. Res. Nat. Bur. Stand.*, 1947, **38**, 191), and that for but-1-ene is due to Aston *et al.* (*J. Chem. Physics*, 1946, **14**, 74). These assignments for ethylene and propylene have been preferred to those given by Rasmussen and Brattain (*ibid.*, 1947, **15**, 120), for consistency with the A.P.I. results. For *cyclo*hexane the assignment is due to Beckett, Pitzer, and Spitzer (*J. Amer. Chem. Soc.*, 1947, **69**, 2488); for *cyclo*pentane, that of Kilpatrick, Pitzer, and Spitzer (*ibid.*, p. 2483); and for aromatic compounds, those of Pitzer and Scott (*ibid.*, 1943, **65**, 805). That for *cyclo*butane is due to Wilson (*J. Chem. Physics*, 1943, **11**, 369). In *cyclo*pentane, the effect of the degree of freedom concerned with " rotation " of the puckering round the ring has been neglected, and in *cyclo*hexane the effect of anharmonicity in the low-frequency vibrations has also been neglected.

For some of the larger molecules the assignments have involved the use of averaged hydrogen frequencies (for details see the references given). This procedure may be justified to some extent by the agreement between the observed and the calculated thermodynamic properties, and by the way in which the zero-point energies obtained by using averaged frequencies fit in with those of molecules for which all the frequencies have been observed. The correctness of the assumption of averaged values for the C–H stretching vibration cannot readily be checked by the agreement of the calculated with the observed thermodynamic properties, because its contribution to these is small, but it seems unlikely that the averaged value can be wrong by more than 50 cm.$^{-1}$, which would only make a difference of 0·14 kcal. per CH_2 group. In the following discussion significance will not in general be attached to zero-point energy differences as small as this.

The values of the heats of atomisation of the elements in their standard states are those given by Coates and Sutton (*J.*, in the press): for carbon 125·1 kcals./g.-atom at 0° K., 126·3 kcals. at 298·16° K.; for hydrogen, 51·24 kcals./g.-atom at 0° K., 51·71 at 298·16° K.

The values of the fundamental constants quoted by Wagman, Kilpatrick, Taylor, Pitzer, and Rossini (*J. Res. Nat. Bur. Stand.*, 1945, **34**, 143) are used. These are the same as those used in the compilation of the " Tables of Selected Values of Properties of Hydrocarbons ".

Heat Contents.—Before discussing the effect of considering binding energy only, it is of interest, in view of Dewar's speculations (*loc. cit.*), to note the values of the heat content of some hydrocarbons. In Table I are set out (in kcals./mole) values of $H^0_{298\cdot16} - H^0_0$ for a number of compounds.

TABLE I.

No. of C atoms.	*n*-Paraffins.	Branched-chain paraffins.	*cyclo*-Paraffins.	1- Mono-olefins.	Aromatics.
1	2·40	—	—	—	—
2	2·86	—	—	2·53	—
3	3·51	—	2·74	3·26	—
4	4·65	4·28 (*iso*butane)	3·24	4·22	—
5	5·67	5·03 (*neo*pentane)	3·60	5·36	—
6	6·99	5·94 (2 : 2-dimethylbutane)	4·24	6·38	3·40

The heat contents of the *cyclo*paraffins are systematically less than those of the *n*-paraffins, and the heat contents of branched-chain paraffins are also less than those of the isomeric *n*-paraffins. This effect is the expected one. The results for the olefins show that, in general, the heat content of *cyclo*paraffins is less than that of open-chain hydrocarbons with the same number of atoms. This raises an interesting point in connection with *cyclo*hexane. It has been pointed out (Cottrell and Sutton, *loc. cit.*) that bond energies obtained from *n*-paraffins at 298·16° K. give the heat of formation of *cyclo*hexane exactly. Without apportioning energy between the C–C and C–H bonds, we can make an equivalent statement by pointing out that at 298·16° K. the increment per CH_2 group to the heat of formation from the elements in their standard states of *n*-paraffins is 4·926 kcals., and, if bond energies are additive, that the heat of formation of *cyclo*hexane should be 6 × 4·926 or 29·56 kcals., in good agreement with the observed value of 29·43 ± 0·19 kcals. At 0° K. the constant increment per CH_2 group in the *n*-paraffins is 3·673 kcals., and on the basis the heat of formation of *cyclo*hexane should be 22·04 kcals., whereas it is in fact 20·01 kcals. Thus *cyclo*hexane is less stable per CH_2 group, and therefore, presumably per bond, than *n*-hexane at 0° K. The chemical significance of this difference will be discussed when we consider the binding energies themselves.

Zero-point Energies.—The zero point energies of the compounds considered are given in Table II. One general result is seen from the table: the zero-point energy of branched-chain isomers is less than that of unbranched compounds. Thus part of the " Rossini effect " of the increased stability of branched-chain hydrocarbons is due to zero-point energy differences. In no case, however, does the zero-point energy account for as much as half the discrepancy. The

TABLE II.

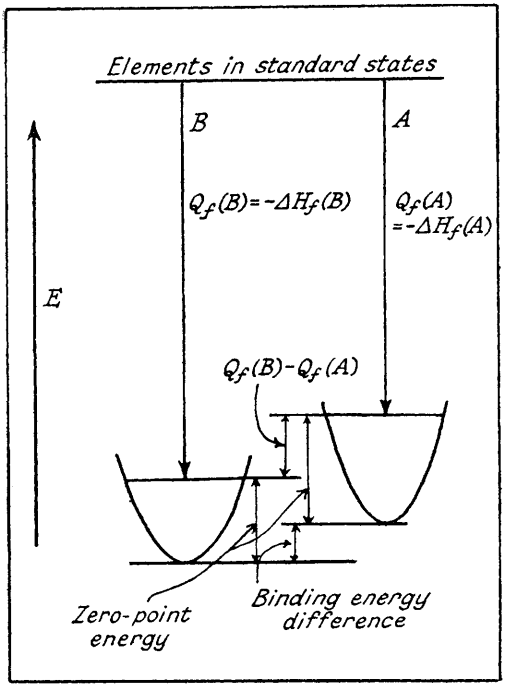
Paraffins.		*cyclo*Paraffins.		Olefins.		Aromatics.	
Compound.	Zero-pt. energy (k.cals.).	Compound.	Zero-pt. energy (kcals.).	Compound.	Zero-pt. energy (kcals.).	Compound.	Zero-pt. energy (kcals.).
Methane	27·1	*cyclo*Propane	49·1	Ethylene	30·5	Benzene	61·7
Ethane	45·2	*cyclo*Butane	67·3	Propylene	48·4	Toluene	78·5
Propane	63·0	*cyclo*Pentane	86·0	But-1-ene	66·1	*o*-Xylene	96·0
n-Butane	80·6	*cyclo*Hexane	104·5	*cis*-But-2-ene	65·9	*m*-Xylene	95·2
*iso*Butane	80·2	—	—	*trans*-But-2-ene	65·6	*p*-Xylene	95·5
n-Pentane	98·5	—	—	*iso*Butene	65·5	—	—
*neo*Pentane	96·8	—	—	—	—	—	—
n-Hexane	116·2	—	—	—	—	—	—
2 : 2-Dimethylbutane	114·5	—	—	—	—	—	—

TABLE III.

Compound (A).	Compound (B).	$Qf_{0^\circ\,\mathrm{K.}}$ (B) − $Qf_{0^\circ\,\mathrm{K.}}$ (A) (kcals.).	Zpt. E (A) − Zpt. E (B).	Percentage of effect due to zero-point energy.
n-Butane	*iso*Butane	1·27	0·4	31
n-Pentane	*neo*Pentane	4·03	1·7	42
n-Hexane	2 : 2-Dimethyl-butane	3·63	1·7	47
But-1-ene	*cis*-But-2-ene	1·36	0·2	15
,,	*trans*-But-2-ene	2·64	0·5	19
,,	*iso*Butene	3·49	0·6	17

comparison is set out in Table III, and in the form of a schematic energy level diagram in the figure. In the first colums the *n*-compound used as reference is given, and in the second, the branched-chain compound to be compared with it. In the third column the difference in heats of formation at 0° K. is given. The notation used is that $Qf_{T^\circ\,\mathrm{K.}}$ represents the heat *evolved* when the compound concerned is formed from its elements in their standard states at T° K. The symbol $AQf_{T^\circ\,\mathrm{K.}}$ refers to the heat of formation from atoms. In the fourth column the zero-point energy difference is given; in the last, the percentage of the effect which can be accounted for by the zero-point energies. Although little exact quantitative significance can be attached to these figures, they do show that an appreciable part of the effect is accounted for. Wolkenstein (*loc. cit.*) gives similar results for butane and pentane, but his estimate of the proportion of the Rossini effect accounted for differs from that given here.

Schematic representation of energy levels in hydrocarbons (*cf. Table III*).



It is noteworthy that the increment in zero-point energy per CH_2 group is approximately constant: in the *n*-paraffin series to *n*-hexane, it is 18·1, 17·8, 17·6, 17·9, 17·7 kcals. It is of interest that the *cyclo*paraffins and the mono-olefins, both of which have the general formula C_nH_{2n}, have very nearly the same zero-point energies; they differ only by about 1·5% for $n = 3$ and $n = 4$.

Binding-energy Terms.—To obtain binding-energy terms, the same procedure is followed as was used by Coates and Sutton (*loc. cit.*) for bond-energy terms. They are given relative to atomic carbon in the ^3P state.

(*a*) C–C and C–H. We have the following figures (in kcals.) for the *n*-paraffins :

	$AQf_{0^\circ\,\mathrm{K.}}$.	Binding energy.	Binding-energy terms (Sum).		$AQf_{0^\circ\,\mathrm{K.}}$.	Binding energy.	Binding-energy terms (Sum).
Methane	346·1	373·2	370·6	*n*-Butane	1036·1	1116·7	1117·3
Ethane	574·2	619·4	619·5	*n*-Pentane	1267·7	1366·2	1366·2
Propane	804·7	867·7	868·4	*n*-Hexane	1498·9	1615·1	1615·1

From the figures in the second column the binding energies (C–C) = 63·6 kcals., (C–H) = 92·65 kcals. are deduced. The total binding energies calculated by using them are given in the third column; apart from that of methane, the binding energies of the compounds are given satisfactorily by using these terms.

(*b*) C=C. If the C–C and C–H energies are assumed constant, we have for the C=C energy term : in propylene 103·2, in but-1-ene 102·9, and in *cis*-but-2-ene 104·1. In the higher 1-olefins, the C=C term is very nearly the same as that in propylene. Using these binding energy terms, we may discuss resonance energies in aromatic compounds and " steric strain ".

Resonance Energies of Aromatic Compounds.—We have the following data :

	$AQf_{0^\circ\,\mathrm{K.}}$	Binding energy.	Sum of binding-energy terms.		Resonance energy.	
			(*a*).	(*b*).	(*a*).	(*b*.
Benzene	1034·0	1095·7	1056·3	1059·0	39·4	36·7
Toluene	1268·1	1346·6	1305·2	1310·6	41·4	36·0
o-Xylene	1502·1	1598·1	1554·1	1561·3	44·0	36·8
m-Xylene	1502·3	1597·5	1554·1	1561·3	43·4	36·2
p-Xylene	1502·1	1597·6	1554·1	1561·3	43·5	36·3

In the colums headed (*a*) are listed the sums of the binding energy terms with $E(\mathrm{C{=}C})$ given the value for the double bond in 1-mono-olefins. In those headed (*b*) corrections have been applied for " substitution effect ", as described by Cottrell and Sutton (*loc. cit.*). Where binding energies were not available for the relevant olefins, it was assumed that about one-third of the substitution effect was due to zero-point energy differences (cf. Table III). In these circumstances no great significance is to be attached to the actual figures quoted : they serve merely to indicate that the use of binding energies instead of bond energies in discussing resonance in aromatic compounds makes no difference to the trend of the results, and leaves the " resonance energies " almost unchanged numerically. Deitz (*loc. cit.*) suggested that if bond energies were corrected for zero-point energies and in addition a cross interaction between hydrogens attached to the same carbon was taken into account, the resultant bond energies would be additive. The surprising result emerged from this treatment that benzene had no resonance energy. It is obvious from the above that consideration of zero-point energy alone does not lead to that result.

Steric Strain.—A full discussion of steric strain in saturated cyclic hydrocarbons requires a more detailed examination than is at present possible (cf. Kilpatrick, Pitzer, and Spitzer, *loc. cit.*; also Pitzer, *Science*, 1945, **101**, 672). At the present stage, however, it is of interest to point out that consideration of binding energies instead of heats of formation at room temperature makes little difference to an estimate of steric strain in these compounds. Below are given (in kcals./mole) the heats of formation from atoms per CH_2 group of three cyclic hydrocarbons, and the binding energies of the same compounds : in each case the corresponding energy increment for the normal paraffins is given for comparison.

	$AQf(\mathrm{g})_{298\cdot1^\circ\,\mathrm{K.}}$ per CH_2.	Binding energy per CH_2.		$AQf(\mathrm{g})_{298\cdot1^\circ\,\mathrm{K.}}$ per CH_2.	Binding energy per CH_2.
n-Paraffin	234·6	248·9	*cyclo*Pentane	233·4	247·0
*cyclo*Hexane	234·6	248·3	*cyclo*Propane	225·5	238·3

It is seen that the effect on strain energy per CH_2 group in the different compounds is slight. There is, however, one effect which appears to be significant : the binding-energy data show " strain " in *cyclo*hexane, an effect which does not appear in the ordinary heat of formation. This effect, as has been pointed out already, is due mainly to the heat content, and not to the zero-point energy, and is therefore certainly real. In this connection, it is interesting that Walsh (*Trans. Faraday Soc.*, 1946, **42**, 779), who has suggested a relation between ionisation potential and bond order, has noted that the first ionisation potential of *cyclo*hexane occurs considerably below that for ethane, and that *cyclo*hexane begins to absorb at longer wave-lengths than ethane in a comparable pressure range. Ramsay and Sutherland (*Proc. Roy. Soc.*, 1947, *A*, **190**, 245) have calculated the skeletal frequencies of *cyclo*hexane on simple valence force field, and find that the C–C stretching force constant is $3{\cdot}7 \times 10^5$ dynes/cm., compared with $4{\cdot}5 \times 10^5$ dynes/cm. in ethane. Partington (unpublished results) has shown that, although values for the activation energy for the thermal decomposition of both ethane and *n*-hexane in the presence of nitric oxide (when reaction chains are inhibited) are approximately equal, and are about 74 kcals., yet that for *cyclo*hexane under similar conditions is 2 kcals. less. The relation of this last observation to the bond energy in *cyclo*hexane is not clear, since the reaction probably does not involve the direct fission of a C–C bond (Staveley, *Proc. Roy. Soc.*, 1937, *A*, **162**, 557) but it does indicate that in some way *cyclo*hexane is less stable than the corresponding normal hydrocarbon.

The author wishes to thank Dr. L. E. Sutton for advice and encouragement, and Imperial Chemical Industries Ltd., Explosives Division, who made it possible for him to carry out this work.

THE PHYSICAL CHEMISTRY LABORATORY, OXFORD.

[*Received, February 5th,* 1948.]