268. *Dissociation Constants, Activation Energies, and Resonance.*

By H. O. Jenkins.

In an important review of dissociation constants (Dippy, *Chem. Reviews*, 1939, **25**, 151), an appendix gives all the accurate data known for monocarboxylic acids, bases, and phenols. In the present paper an attempt is made to interpret those data, the concept of quantum-mechanical resonance being used.

Many compounds exist for which a single valency bond structure does not adequately represent the properties; *e.g.*, the usual formula for acetic acid does not account for its acid properties as compared with methyl alcohol (Pauling, *Proc. Nat. Acad. Sci.*, 1932, **18**, 293). The development of quantum mechanics has partly removed such difficulties by the introduction of the concept of resonance between molecular states, to each of which corresponds a valency-bond diagram with the electrons generally in closed localised pairs. Pauling's method considers the molecule as a superposition of a number of canonical structures, the energy of the molecule being lower than that of any one structure as a result of the coupling interactions, and the fall in the energy (from an arbitrary non-equilibrium position) being called the resonance energy of the molecule.

In this paper, although we use valency-bond diagrams we are really concerned with the stability of states, the relative values of the coefficients, and the number of terms which must be taken into account in the approximate wave equations for the molecules of certain organic acids and bases. For data, dissociation constants and activation energies will be used. Heat data, internuclear distances, force constants, and electric dipole moments in addition to dissociation constants have already been used successfully in this connection by Pauling (see " The Nature of the Chemical Bond," Cornell, 1939), Sutton, Brockway, and others.

It is now well recognised that a rough relation of some sort exists between complexity of degeneracy, which we shall define in terms of the number of principal resonating structures (n), and resonance energy relative to one canonical structure. It is, of course, realised that the less important structures, such as the Dewar benzene structures, each make their contribution to the state of the molecule, but to a first approximation we are justified in ignoring them. Hence, n will be taken as 2 for benzene, 3 for naphthalene, 4 for anthracene, 5 for chrysene and so on. Sidgwick (J., 1937, 694) gives a table of resonance energies derived from combustion data, and shows that for these four molecules, the resonance energy per ring is roughly constant; *i.e.*, the energy increases regularly with n. Again, Lennard-Jones and Coulson (*Trans. Faraday Soc.*, 1939, **35**, 822) give the resonance energies relative to m double bonds for the first four members of the free-radical series $C_{2m+1}H_{2m+3}$, and inspection reveals the regular rise with n. In fact, for these free radicals linear relation exists between n and resonance energy. Now, since resonance energies are not always available, we shall use the number of principal structures as a measure of the resonance energy and shall show that extremely simple relations exist between n, or some function of n, and dissociation constants and activation energies.

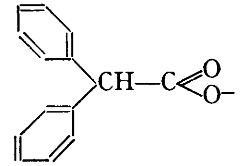
The Dissociation Constants of Acids.—Consider the series of acids, methyl alcohol, acetic, phenylacetic, and diphenylacetic acid, of which the strengths (Dippy, *loc. cit.*) are given below. The increase in strength when phenyl is introduced into a saturated aliphatic acid has generally been referred to an inductive effect ($-I$). Dippy (*loc. cit.*, p. 178) states that the relative strengths of vinylacetic, phenylacetic, and diphenylacetic acids lead inevitably to the conclusion that the ethenyl and the phenyl group possess an intrinsic attraction for electrons. It is also said that dipole-moment measurements verify the existence of such an effect; *e.g.*, the dipole moment of ethyl bromide is 2·09 D. whereas that of vinyl bromide is only 1·48 D.

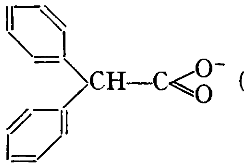
Acid.	$K \times 10^5$.	n.	$a\,(n-1)$.	Acid.	$K \times 10^5$.	n.	$a\,(n-1)$.
$CH_3{\cdot}OH$	0·00	1	0·00	$CHPh_2{\cdot}CO_2H$	11·55	8	11·41
$CH_3{\cdot}CO_2H$	1·75	2	1·63	$CPh_3{\cdot}CO_2H$	25 *	16	24·4
$CH_2Ph{\cdot}CO_2H$	4·88	4	4·89				

* Extrapolated.

Many years ago Sutton (*Proc. Roy. Soc.*, 1931, **133**, 668) ascribed the differences in the moments of phenyl and *tert.*-butyl compounds, $\mu_{\text{ar.}} - \mu_{\text{al.}}$, to a mesomeric shift of electrons. Electron-diffraction investigations have, however, established the fact that chlorobenzene has a carbon–chlorine link of partial double-bond character, and doubtless vinyl bromide would show the same effect. It then follows that at least part of the reduction in moment (absolute value) as we proceed from, say, *tert.*-butyl chloride to chlorobenzene is due to the shortening of the bond, which may amount to 0·1 A. This, however, involves the problem of the form and magnitude of $d\mu/dr$. Now the dipole moments of toluene, diphenylmethane, and triphenylmethane are all near 0·5 D. (*Trans. Faraday Soc.*, 1934, Table of Dipole Moments), indicating that the $-I$ effect of phenyl groups is extremely small and certainly not sufficient to raise the dissociation constant of diphenylacetic acid to $11{\cdot}55 \times 10^{-5}$ from $1{\cdot}75 \times 10^{-5}$, the value for acetic acid. (The sign of the dipole moment of toluene is not readily explained: the relative electronegativities of carbon and hydrogen would seem to require an electric moment in the opposite direction.) The quantum-mechanical method of approach, concentrating as it does on energy relationships, is much more fruitful. Just as acetic acid owes its strength over and above that of methyl alcohol to the superposition of completely degenerate eigen-functions, so the greater enhancement of strength in phenyl- and diphenyl-acetic acids must have its origin in the increase in resonance energy due to the greater number of canonical structures. For instance, in diphenylacetic acid, we can see that the undissociated molecule, though possessing considerable resonance energy, has components incompletely degenerate, and it is possible that the symmetry of the ion permits complete resonance, between structures such as (I) and (II), their energy difference being considerably less than the resonance energy. It must be confessed that no simple picture of the interaction can be given. A linear relation has been shown to exist between K and n for these compounds (H. O. Jenkins, *Nature*, 1940, **145**, 149), and the equation to the line (in terms of 10^{-5}) is

(I.)





(II.)

$$K = -1{\cdot}63 + 1{\cdot}63n$$

or

$$K = a\,(n-1), \text{ where } a = 1{\cdot}63$$

and in terms of free-energy changes

$$-RT\ln K = -RT\ln a - RT\ln(n-1)$$

This may mean that there is an extra decrease in free energy of $2{\cdot}303RT\log(n-1)$ because of the gain in resonance energy during ionisation, the unsymmetrical dissociated molecule changing into the symmetrical configuration of the ion. If ΔE_r is the change in resonance energy relative to the undissociated molecule, we have

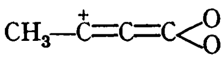
$$\Delta E_r = 1380 \log_{10} K_s/K_u$$

where K_u refers to acetic acid and K_s to the substituted acetic acids, whence $\Delta E_r = 0{\cdot}68$ and 1·1 kg.-cals. for phenyl- and for diphenyl-acetic acids respectively.

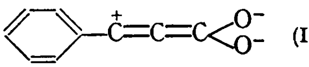
Extrapolation of the linear relation suggests a dissociation constant of $2{\cdot}5 \times 10^{-4}$ at 25° for triphenylacetic acid in water, but solubility difficulties have prevented its measurement. In these acids the component structures are all of equal stability, the coefficients in the approximate wave equation being equal, and it being necessary to take into account at least *n* terms.

Another instance of the enhancement of the dissociation constant by resonance is afforded by tetrolic ($K = 222{\cdot}8 \times 10^{-5}$) and phenylpropiolic acids ($K = 590 \times 10^{-5}$). The ratio K_2/K_1 is 2·65, whereas the ratio of the strengths of phenylacetic and acetic acids is nearly the same, *viz.*, 2·79. It is suggested that the same explanation holds good. The greater acidities found in these triple–single-bonded structures are probably due to resonance with charged double–double-bonded structures such as (III) and (IV). Also, because of

(III.)

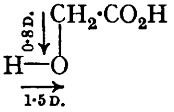


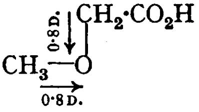
$CH_3-\overset{+}{C}=C=C\begin{smallmatrix}O^-\\O^-\end{smallmatrix}$

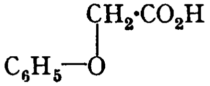


(IV.)

the Kekulé resonance in the benzene ring, any value given to *n* for tetrolic acid must be multiplied by 2 for phenylpropiolic acid. Similar explanations to the above account for the greater strength of vinylacetic ($4{\cdot}62 \times 10^{-5}$) than of butyric acid ($1{\cdot}50 \times 10^{-5}$), of allylacetic ($2{\cdot}11 \times 10^{-5}$) than of valeric acid, of benzoic ($6{\cdot}27 \times 10^{-5}$) than of *cyclo*hexanecarboxylic acid ($1{\cdot}34 \times 10^{-5}$), and of phenylacetic ($4{\cdot}88 \times 10^{-5}$) than of *cyclo*hexylacetic acid ($2{\cdot}36 \times 10^{-5}$). The strengths of glycollic, methoxyacetic, and phenoxyacetic acids, *viz.*, $K \times 10^5 = 15$, 33·5, and 73·5, respectively, present an interesting problem :

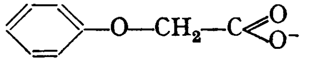


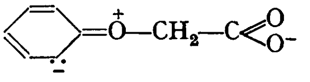




Dippy (*loc. cit.*, p. 172) states that, contrary to expectation, methyl, when it displaces hydrogen of the hydroxyl group, causes an increase in acid strength. A definite weakening is anticipated on introduction of methyl, which is regarded as having a + *I* effect. This evidence for the polar effect of methyl came from the dipole moments of *p*-substituted toluenes. It must, however, be recognised that the sign and magnitude of the bond moment depend on the relative electronegativities of the atoms concerned. Remembering this, the dissociation constants of glycollic and methoxyacetic acids need not cause any surprise since $\mu_{\text{H-O}} = 1{\cdot}5$ D. and $\mu_{\text{C-O}} = 0{\cdot}8$ D., the more positive atom coming first. Simple vector analysis indicates that the dissociation constant of the methoxy-acid should be roughly twice that of glycollic acid. However, the strength of phenoxyacetic acid cannot be accounted for on the basis of inductive effects alone. Methoxy- and phenoxyacetic acids are alike, apart from the possession by the latter of a ring structure in which a Kekulé-like resonance is possible. This doubles the number of resonating states contributing to the structure of the latter ion. Thus we arrive at some understanding of its stability compared to that of the methoxyacetic ion. It is also very probable that in addition to such structures as (V), structures such as (VI) contribute to the normal state of the ion.

(V.)

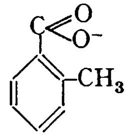


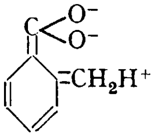


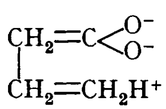
(VI.)

In the methoxy-acid, resonance with a double-bonded structure $—O{=}CH_3$ is not possible since the carbon atom has only four orbitals available for bond formation. We would not expect the charged structures to be as stable as the uncharged ones, and hence they will make a smaller contribution to the molecular state, *i.e.*, their coefficients in the wave equation will be smaller.

Considerations of this kind are pertinent in discussing many ortho-acids. There is some justification in the bulk hypothesis in so far as bulky groups are often hybrids. The high strength of *o*-toluic acid may be due to resonance between such structures as (VII)

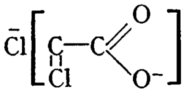

(VII.)

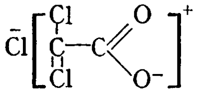

(VIII.)

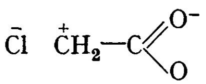

(IX.)

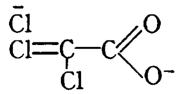
and (VIII). This is, of course, the hydrogen-bond formation postulated by Dippy and his co-workers (J., 1937, 1421), defined a little more precisely. Its existence could be detected if the carbon–methyl bond distance could be measured in *o*-toluic acid by electron diffraction or otherwise. The recent spectroscopic and electron-diffraction work on methylacetylene is suggestive (Herzberg, Patat, and Verleger, *J. Physical Chem.*, 1937, **41**, 123; Badger and Bauer, *J. Chem. Physics*, 1937, **5**, 599; Pauling, Springall, and Palmer, *J. Amer. Chem. Soc.*, 1939, **61**, 927). The C–CH_3 distance in this compound is 0·08 A. less than that required for a pure single bond, suggesting the existence of H^+ $CH_2{\equiv}C\cdots\cdot$ types of structure contributing to the state of molecule. Structures such as (IX) probably contribute to the structure of the butyric acid molecule ion and account for its relatively high dissociation constant. H. O. Jenkins and Dippy (*J. Amer. Chem. Soc.*, 1940, **62**, 483) have put forward a relation between length of chain and dissociation constant for the aliphatic acids, $C_nH_{2n+1}\cdot CO_2H$, *viz.*, $\log K = a + b/r^6$, where r is the distance between the end carbon atom and the carbon of the carboxyl group. This relation does not hold for the anomalous butyric acid, a much smaller r being required than that calculated. The present postulated double-bonded structures do something to reduce the effective r.

The strengths of the chloroacetic acids will now be considered; the relevant data are: $CH_2Cl\cdot CO_2H$, $K = 1{\cdot}4 \times 10^{-3}$; $CHCl_2\cdot CO_2H$, $K = 5{\cdot}1 \times 10^{-2}$; $CCl_3\cdot CO_2H$, $K = 1{\cdot}2$. The author has pointed out (*Nature*, 1940, **145**, 625) that all attempts to account for these dissociation constants on the basis of inductive effects alone are doomed to failure since the resultant group moments of one, two, and three C–Cl groups are μ_{Cl}, $2\mu_{Cl}\cos\frac{1}{2}\theta$, and $\mu_{Cl}\,(6\cos\theta + 3)^{\frac{1}{2}}$, respectively, θ being the tetrahedral angle, and dipole interaction being neglected. However, resonance with such structures as (X) and (XI) preferentially stabilises the ions of these acids.


(X.)

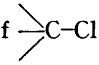
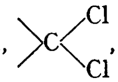
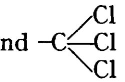

(XI.)


(XII.)


(XIII.)

There are two ways of counting the number of resonating structures. If ionic structures such as (XII) containing tervalent carbon and probably of low stability are not included, we obtain the numbers 2, 6, and 14 for the mono-, di-, and tri-chloroacetic acids, respectively. On the other hand, if they are included we get the numbers 4, 10, and 20. There are, *e.g.*, twelve structures of the type (XIII).

If the first set of numbers is taken, the linear relation between log K and log n is shown in Fig. 1. However, an equally good straight line can be drawn if the second set of numbers is taken instead, and log K is plotted against log n, or even against n. This latter method of plotting may prove to be of the greater theoretical significance. We would not expect acetic acid to come on any of these straight-line relations. Superimposed on the resonance effect is the classical inductive effect.

We are comparing compounds in which the inductive effect is roughly the same. The group dipole moments of , , and  are roughly the same.

It has already been suggested by Gregg, Hampson, Jenkins, Jones, and Sutton (*Trans. Faraday Soc.*, 1937, **33**, 852) that hybridisation occurs in such molecules as benzyl chloride and benzotrichloride from an examination both of orienting power and of the dipole-moment evidence. Toluene only gives 4% of the *m*-derivative on nitration, whereas benzyl chloride gives 12—15·5%, and benzotrichloride 64·5—74·8%. Again, the dipole moment of benzotrichloride is 2·07 D., whereas that of ααα-trichloroethane is only 1·57 D. (Sutton, *Proc. Roy. Soc.*, 1931, **133**, 668). Further evidence necessitating the existence of this type of charged structure involving double-bonded halogen (*e.g.*, in ) has been published by Brockway and H. O. Jenkins (*ibid.*, 1936, **58**, 2036) and Gregg, Hampson, *et al.* (*loc. cit.*). It can be taken as reasonably certain that hybridisation occurs in the ions of the chloroacetic acids. Further evidence for this is given later (p. 1452).

FIG. 1.

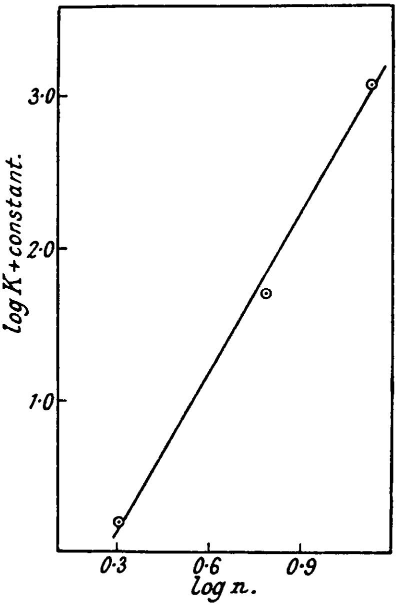
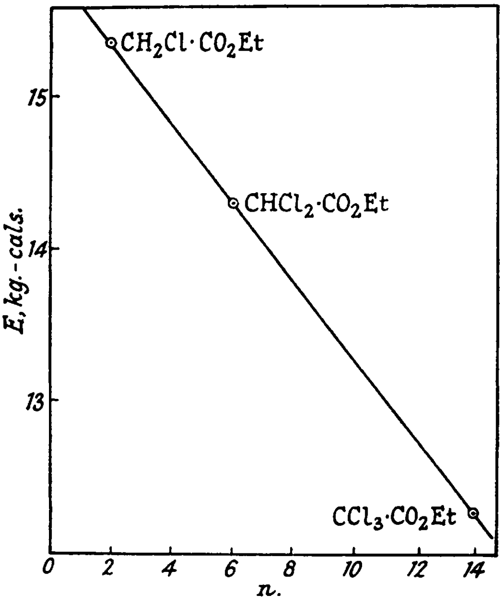
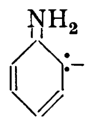
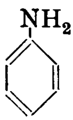


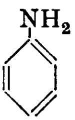
FIG. 2.



The Dissociation Constants of Bases.—Similar reasoning will account for the strengths of many nitrogenous bases, with, however, the important proviso that it is the un-ionised molecule possessing a lone pair of electrons on the nitrogen atom which is preferentially stabilised by resonance. A linear relation has already been shown to exist between p_{K_B} and log *n* for ammonia, aniline, diphenylamine, and triphenylamine (H. O. Jenkins, *Nature*, 1940, **145**, 149). The relevant data are given below. The equation to the line is p_{K_B} = 9·27 — 6·9 log *n*, charged structures such as (XIV), being less important than (XV) and (XVI).

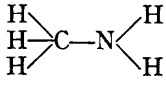

(XIV.)


(XV.)

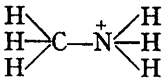

(XVI.)

Base.	p_{K_B}.	*n*.	log *n*.	Base.	p_{K_B}.	*n*.	log *n*.
NH_3	9·27	1	0·000	$NHPh_2$	0·85	16	1·204
NH_2Ph	4·62	5	0·699	NPh_3	0·00	$\gg$30	—

Another series of bases which find their interpretation on these lines is ammonia ($K_B = 1·79 \times 10^{-5}$), methylamine ($K_B = 43·8 \times 10^{-5}$), dimethylamine ($K_B = 52·0 \times 10^{-5}$), and trimethylamine ($K_B = 5·45 \times 10^{-5}$). Here we immediately notice that the symmetrical molecules, ammonia and trimethylamine, are the weakest, suggesting that these undissociated molecules have more ionic resonance energy than the other amines. When methyl is introduced into ammonia, the powerful increase in strength is to be ascribed to a decrease in symmetry in the undissociated molecule which possesses a pyramidal structure and to the development of tetrahedral symmetry in the ion :



Undissociated molecule.



Ion.

The carbon and the positive nitrogen appear to be indistinguishable and thus the ion has the ethane type of symmetry.

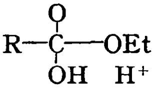
Activation Energies involved in Acid Hydrolyses of Chloroacetic Esters.—Timm and Hinshelwood (J., 1938, 862) have determined the parameters *PZ* and *E* of the Arrhenius equation, $k = PZe^{-E/RT}$, for the acid hydrolyses of the three chloroacetic esters in 55·7% alcohol. The *PZ* factor increases with *E* as substitution proceeds; *k* varies only slightly for the three reactions, but the activation energy decreases systematically, and this, it is stated, is in accordance with expectations based on the application of the electronic theory. It may be pointed out that the inductive effect will not explain this systematic decrease in activation energy (see section on the dissociation constants of acids).

Modern theories of reaction velocity are characterised by an attempt to correlate Arrhenius parameters with molecular structure. It is thus probable that the decrease of *E* as successive chlorine atoms are introduced into the ester molecule bears some relation to the molecular structures involved. Support for this view comes from what has been said about dissociation constants if we remember that rate constants and equilibrium constants are closely related (Brönsted and Pedersen, *Z. physikal. Chem.*, 1924, **108**, 185; Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 96; Dippy and Watson, J., 1936, 436). A relation such as $\log k = a \log K + b$ is very often found, and this is not surprising when we remember that the transition-state method of dealing with reaction velocities uses statistical theory to calculate the equilibrium constant of a transition complex of reacting substances. The close connection between equilibrium and velocity constants suggested trying a plot of activation energy against number of canonical structures, and again a relation is found (see Fig. 2). The relevant data are given below.

Ester	$CH_2Cl{\cdot}CO_2Et$	$CHCl_2{\cdot}CO_2Et$	$CCl_3{\cdot}CO_2Et$
E	15,350	14,300	12,280
n	2 or 4	6 or 10	14 or 20

All the points lie on a straight line to within 40 cals., no matter which set of numbers (2, 6, 14; or 4, 10, 20) is used, and this implies remarkably accurate experimental work. The same numbers which account for the rise in dissociation constant also account for the decrease in activation energy in the hydrolyses of the corresponding esters.

The usual interpretation of the acid hydrolysis of an ester is that of the Lowry mechanism. A hydroxyl ion is obtained from water, a proton from the acid catalyst, and the transition complex (XVII) is obtained. The last step involves the breaking of the C–OEt bond to form EtOH (Polanyi and Szabo, *Trans. Faraday Soc.*, 1934, **30**, 508). It is the charge on the carbonyl carbon that plays the decisive part in determining the energy of activation. The linear relation may owe its origin to the fact that each canonical structure helps to pile up positive charge on this carbon atom.



$$R-\overset{O}{\underset{OH}{C}}-OEt \quad H^+$$

(XVII.)

Evans and Polanyi (*ibid.*, 1937, **34**, 11) have shown that perturbation energy between two states ψ_1 and ψ_2 may act as a driving force and contribute to the lowering of activation energy. The hydrolysis being expressed as

$$\underset{(A)}{OH^-} + \underset{(BC)}{R{\cdot}CO_2Et} \longrightarrow \underset{(B)}{R{\cdot}COO^-} + \underset{(AC)}{EtOH}$$

then the energy of the system for any configuration can be shown to be either $E_1 = B_1 + R_1$, or $E_2 = B_2 + R_2$, where B_1 is a bond energy in the molecule $R{\cdot}CO_2Et$ and *R* is the repulsion energy between $R{\cdot}CO_2Et$ and OH^-; B_2 and R_2 are corresponding terms for the second state. When E_1 and E_2 approach one another, perturbation results. When they are both equal to E_i, the two energy values for the system are $E_i + E_{12}$ and $E_i - E_{12}$. The transition state is that for which E is a minimum, and the activation energy is $(E_i)_m - E_{12}$. It is suggested that the resonance energy in the transition state systematically increases, and lowers the activation energy correspondingly. This lowering of E is related to such phenomena as the resonance of the p_h electrons in triphenylmethyl furnishing the driving energy in the dissociation of hexaphenylethane into free radicals (Pauling and Wheland, *J. Chem. Physics*, 1933, **1**, 362; Huckel, *Trans. Faraday Soc.*, 1934, **30**, 40), and also to the fact that such a small heat of transformation is needed to change diamond into graphite, energy being gained by the resonance of the p_h electrons in the hexagonal graphitic planes.

[*Note, added July* 23*rd*, 1940.] Everett and Wynne-Jones (*Trans. Faraday Soc.*, 1939, **35**, 1380) have criticised the practice of regarding the dissociation constant of an acid in water at 25° as a measure of its intrinsic strength on account of the known solvent and temperature dependence. *Inter alia* their treatment is based on the questionable assumption of the temperature invariance of ΔC_p. A refutation of certain of their claims will shortly be made by Dr. J. F. J. Dippy and the author, but here it may be stated that second-order solvent–temperature effects do not affect the main conclusions reached in this paper. It cannot be fortuitous that dissociation-constant data at 25° have been found to reveal well-defined regularities, which can be correlated with many other fields of investigation. Moreover, Wynne-Jones's relationship log K/K_s–$1/\varepsilon$ (*Proc. Roy. Soc.*, 1933, **140**, *A*, 440) has been tested satisfactorily upon data at a *fixed* temperature.

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