

system contributes mainly to the change of the value of the absorption coefficient at the long-wave side, the continuum mainly to that at the short-wave side. The contribution of the continuum is much larger than that of the band system on account of the steep slope of the upper $U: r$ curve for this region.

Similar pressure effects have been studied quantitatively by Kondratjew and Polak³ with whose results ours agree. It appears therefore unnecessary to go into the details of these experiments at greater length, but attention should be drawn to the fact, that the change of the absorption coefficient with pressure may be understood without resort to the reactivity of the gases.

C. M. BHASKER RAO.

R. SAMUEL.

Department of Physics,
Muslim University,
Aligarh.
April, 25, 1936.

¹ N. R. Dhar and P. N. Bhargava, *Nature*, Dec. 1, 1934.

² N. R. Dhar and P. N. Bhargava, *Ind. J. Phys.*, 1936, 19, 43.

³ V. Kondratjew and L. Polak, *Phys. Zs. (Sowjet-union)*, 1933, 4, 764 and literature mentioned there.

On the Constitution of Formic Acid and Formates.

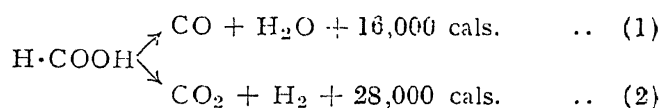
FURTHER to my communication¹ on the subject I wish to add the following. I have since been in touch with Prof. Wheeler, who has very kindly given me full details of his calculations of parachor values which I quote for convenience:—

C, 4.8; H attached to carbon, 17.1; H attached to oxygen, 11.3; O₂ double bond in acids, 60.0; Total, 93.2.

In this calculation it will be seen that Prof. Wheeler, while adopting Sugden's system for the greater part, has taken in places Mumford's values. For example, Sugden's system does not, to my knowledge, differentiate between a hydrogen attached to carbon and that attached to oxygen. Further Hunter and Mass² adopting Sugden's data calculate the parachor value of 102.2 for formic acid of the usual formula, which

is certainly far greater than the one observed. My conclusions based on parachor values do need no alteration.

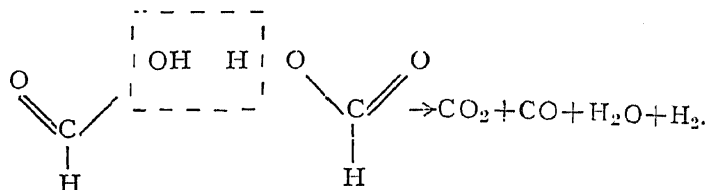
Further support for the view, that the H of CH in formic acid is active is available in the relative rate of decomposition on catalytic surfaces. Formic acid decomposes at 280°C. on glass surfaces according to the scheme



and the rates of decomposition, provided no other factor comes into play, should be

in the ratio of $e^{-\frac{16000}{RT}} \div e^{-\frac{28000}{RT}} = e^{+12}$.

Actually it has been shewn by Hinshelwood and Topley³ that the two reactions proceed with *equal rates* which becomes possible, if the H of the CH group could be adsorbed on the glass surface. Thus



R. M. HALASYAM.

3, Y. M. I. A. Buildings,
Armenian Street, Madras.

¹ *Curr. Sci.*, 1936, 4, 651.

² *Jour. Amer. Chem. Soc.*, 1929, 51, 153.

³ *Proc. Roy. Soc.*, 1922, 100 (A), 575.

Constitution of Formic Acid and Formates.

Isosterism.—This term seems to have been first used by Langmuir.¹ He says "Co-molecules are isosteric if they contain the same number and arrangement of electrons. The molecules of isosteres must, therefore, contain the same number of atoms." Based on this conception he deduces that "when isosteric co-molecules are also isoelectric, that is, when they have the same total charge, all their physical properties should be closely similar." In the case of solid substances, crystal form being one of the characteristic physical properties, isoelectric isosteres should be isomorphous and they have been shown to be so.

Langmuir's idea of isosterism has been correctly used by many with useful results. But there are cases where the term "isosteric" has been wrongly employed and confused with "isoelectronic," that is, containing the same number of electrons.² The formate ion $[\text{CHO}_2]^-$ whatever structure it may be given, cannot be isosteric with the nitrite ion $[\text{NO}_2]^-$ since they do not contain the same number of atoms and the deduction of Ray and Sarkar³ that their salts should be isomorphous is therefore wrong.

Isomorphism.—Unless this phenomenon is understood and studied correctly it cannot be used as a help in elucidating the structure of compounds. A. E. H. Tutton⁴ writes, "An isomorphous series may be defined as one the members of which have some definite chemical analogy and crystallise in the same system and class of symmetry and which develop the same form, the faces of which are inclined at angles which only differ by an amount not exceeding two and a half degrees, the amount being less the greater the symmetry." The first requisite of isomorphism is therefore very close similarity in crystal form. The following data taken from P. Groth's *Chemische Krystallographie*⁵ will show how fundamentally different the structures of Nitrites and Formates are:

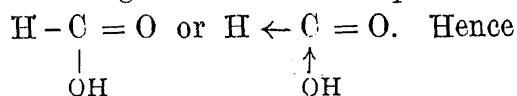
	<i>Nitrite.</i>	<i>Formate.</i>
Sodium	Rhombic	Monoclinic Prismatic
Calcium	Hexagonal	Rhombic Bisphenoidal
Strontium	Hexagonal	Rhombic Bisphenoidal
Barium	Hexagonal	Rhombic Bisphenoidal

Mixed crystal formation.—This can serve as a confirmatory evidence of the existence of isomorphism and not as an independent proof of it. Groth⁶ writes, "apparently homogeneous mixed crystals of continuously varying composition are obtainable with substances whose chemical nature is totally different (*i.e.*) the crystals of one substance are capable of taking up another substance not isomorphous with it in varying proportions." Langmuir in the paper already mentioned (p. 1555) says, "The data given in the case of nitrates and chlorates show conclusively in my mind that the formation of mixed crystals often occurs when there is no close resemblance in crystal structure. It seems therefore that this criterion should not be used to indicate similarity in chemical constitution." The only evidence adduced by Ray and Sarkar for the existence of isomorphism between Formates and Nitrites is mixed crystal formation.

It is therefore clear that Halasyam's "unequivocal evidence from Isomorphism of Formates and Nitrites"⁷ does not exist.

Parachor.—Halasyam was not correct when he stated that the dihydroxymethylene form was proposed by me to explain the absence of the Raman line or when he calculated the parachor for this form and criticised that it did not agree with the experimental value for formic acid.⁷ It was never suggested by me that free formic acid is dihydroxymethylene and he evidently assumed that I did so as otherwise his criticisms were not valid. With a view to clear this misunderstanding a more careful perusal of my first letter⁸ was suggested. No objection was raised against the term "labile structure". This form was assumed to be produced in the course of certain reactions. To go further than this at present will not be justifiable.

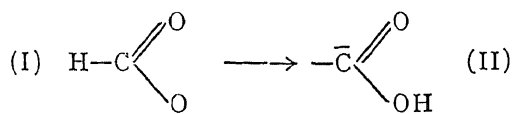
Using either Mumford and Phillips' constants for the parachor of the various atoms and bonds or the more widely accepted values given in Llandolt-Bornstein, formic acid is found to be quite normal and it falls perfectly into line with its homologues. Hence parachor does not support any exceptional formula for formic acid. It will be interesting to note that Mumford and Phillips do not differentiate between single covalent and co-ordinate bonds, both being given the same value ± 0 and hence calculation using their constants gives the same parachor for



Halasyam's preference for the Sarkar and Ray formula is not sound. According to the values given in Llandolt-Bornstein, formic acid can have only the ordinary formula and cannot have co-ordinate bonds. This is further supported by other physical properties such as boiling point, dipole moment, heat of formation, etc.

Raman Spectra.—The question of the Raman spectra has been discussed sufficiently by Venkateswaran.⁹ No support can be found for the theory of Sarkar and Ray that the ionisable hydrogen is not the hydrogen of the hydroxyl group but the one attached to the carbon. It is therefore gratifying to note that these authors have given it up.¹⁰ They agree that formic acid (liquid and aqueous solution), its esters and its salts in the solid state have the normal structure possessing a C-H bond, but express

the opinion that the salts are abnormal in aqueous solution owing to the ion undergoing the prototropic change.



It is possible that isomeric change to form (II) may take place to some extent in the solution and that an equilibrium may exist between (I) and (II). But taking into consideration the relative stability of the two structures it will be difficult to imagine that there could be present more than a very small quantity of (II). Available evidence from Raman spectra indicates that the aqueous solutions of formates are also normal, that is, the formate ion has the C-H bond in the solutions also.

T. R. SESHADRI.

Department of Chemistry,
Andhra University, Waltair.

May 5, 1936.

¹ "Isomorphism, Isosterism and Covalence," *J.A.C.S.*, 1919, **41**, 1543-1558.

² For the use of the word "isoelectronic" see Jevons, *Report on Band Spectra of Diatomic Molecules*, published by the Physical Society, 102.

³ *Nature*, **133**, 646.

⁴ "Crystalline Form and Chemical Constitution," (Macmillan & Co.), 127.

⁵ Wilhelm Englemann, Leipzig.

⁶ *An Introduction to Chemical Crystallography*, translated by Marshall, 97.

⁷ *J. Indian C. S.*, 1935, 813.

⁸ *This Journal*, 1935, **3**, 353-4.

⁹ *This Journal*, 1936, **4**, 736-7.

¹⁰ *Nature*, 1936, 495.

Bauxite-Gypsum Mixtures at High Temperatures.

THERE are extensive deposits of good quality Bauxite and Gypsum in the neighbourhood of coal mines (The Punjab and C. P.). If a process be found to obtain the two most important commodities alumina and sulphuric acid by making use of the above minerals, India could be made independent of foreign imports of these two chemicals. The import of sulphur in 1934 amounted to 20,000 tons worth Rs. 19 lakhs. Experiments made in the authors' laboratories show that by suitably mixing Bauxite and Gypsum (2 to 5) and heating the mixture to 1180°-1200° C., for about eight hours,

all the oxide of sulphur is expelled. This oxide can be used in the manufacture of sulphuric acid. The calcium aluminates formed in the process of roasting, are found to be water soluble and furnish on hydrolysis, pure crystalline alumina.

The results are summarised in the table given below:—

Al₂O₃ in Bauxite = 58.83%. SO₃ in Gypsum = 44.64%.

Proportion of Bauxite to Gypsum	Temperature	Time of heating in hours	Yield of alumina per cent.		Loss of SO ₃ per cent.
			In Acid extract	In Water extract	
1 2 : 3	1080°-1100° C.	8-8½	52.51	3.43	5.01
2 2 : 4	"	"	53.41	19.61	24.78
3 2 : 5	"	"	54.72	30.63	39.87
4 2 : 6	1270°-1280° C.	"	56.63	15.06	44.64
5 2 : 3	1160°-1180° C.	8-8½	56.38	17.36	37.23
6 2 : 4	"	"	57.81	31.38	44.64
7 2 : 5	"	"	58.61	35.43	44.64
8 2 : 3	1230°-1240° C.	8-8½	57.89	28.64	44.64
9 2 : 4	"	"	57.96	36.49	44.64
10 2 : 5	"	"	58.69	35.76	44.64
11 Bauxite alone	1080°-1100° C.	"	1.65
12 Gypsum alone	1270°-1280° C.	"	25.63

Of the 58.8 per cent. of alumina present in Bauxite, 35 per cent. can be leached out by cold water alone. The rest of alumina present in the residue, if treated with a very dilute solution of sulphuric acid, produces aluminium sulphate which can be converted into alum. The residue, left after the extraction of calcium aluminate by water and dilute acid, contains mostly Titanium and Iron as oxides. There is a great demand for titanium oxide as a white paint and the recovery of TiO₂ from this waste residue is engaging the attention of the authors at present. Since the results, so far obtained are promising, it is proposed to carry these operations on a semi-commercial scale. Details of experiments will be published elsewhere.

M. B. RANE.

V. S. DUBE.

M. K. RATNAM.

Chemical Laboratories,
Benares Hindu University,
Benares.

April 11, 1936.