

Felicitations.

THE Birthday Honours list has brought the distinction of Knighthood to two of our editorial co-operators, Dr. M. O. Forster, F.R.S. and Col. R. McCarrison, C.I.E., whom we have pleasure in felicitating. It is highly gratifying to note that scientific service is suitably recognized by His Majesty's Government in India and we hope that other eminent scientific workers in the country will be speedily and fittingly honoured.

As administrator of the Indian Institute of Science which occupies the premier position in India, for the last ten years Sir M. O. Forster has rendered invaluable services in the expansion and consolidation of the research departments under his administrative care and his wide experience and knowledge, his eminent attainments and

above all, his genial and stimulating personality have been a source of inspiration and liberal education to all who have come within the range of his influence.

Sir R. McCarrison is an intrepid researcher in the science of animal nutrition,—with special reference to goitre, and the results of his scientific labours have been internationally recognized. He has been recently elected to open the International Conference on Goitre at Berne and the Knighthood conferred on him is a fitting recognition of his eminence as an investigator of the fundamental problems which affect human welfare. We wish both of our co-operators who are the recipients of distinguished honours, long life of increasing usefulness in the service of science and of the country.

On a Connection between Di- and Triatomic Molecules.

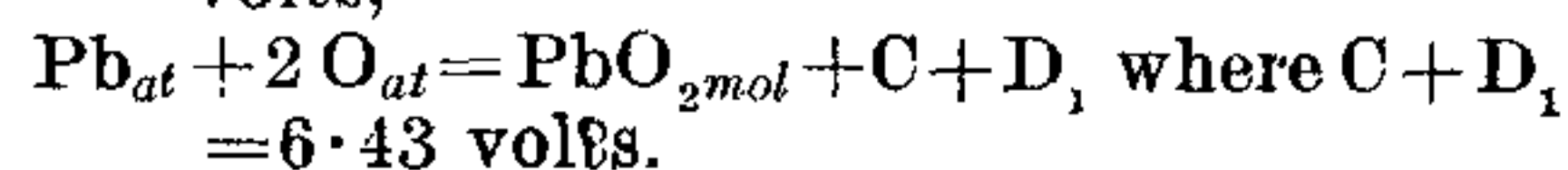
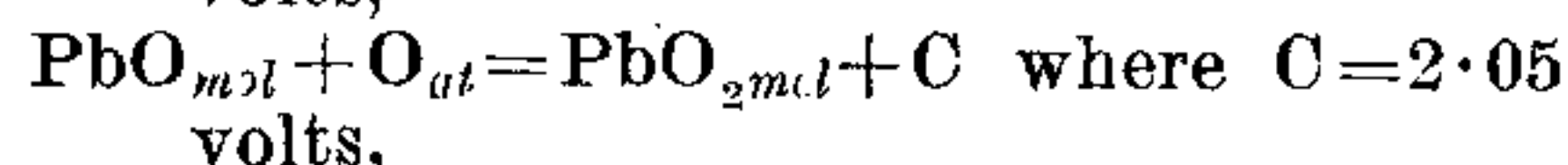
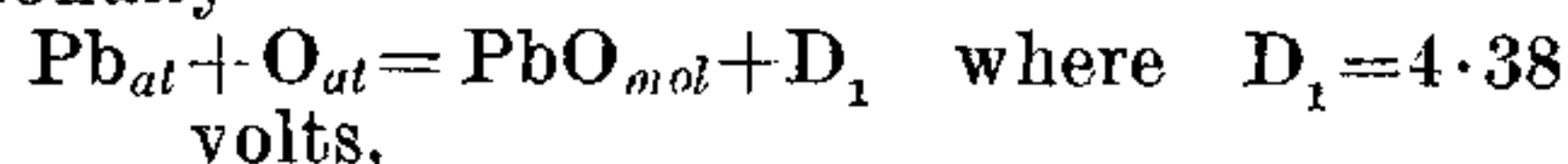
By Dr. H. Lessheim and Dr. R. Samuel,
Muslim University, Aligarh.

SINCE the recent development of the theory of molecular spectra it has become clear that it is necessary to pay consideration to the fact that chemical linkage does not always arise from the ground levels of the atoms concerned. We have therefore to add a certain amount of energy of excitation to the heat of dissociation of a compound in its atoms, if it is taken from thermo-chemical data.

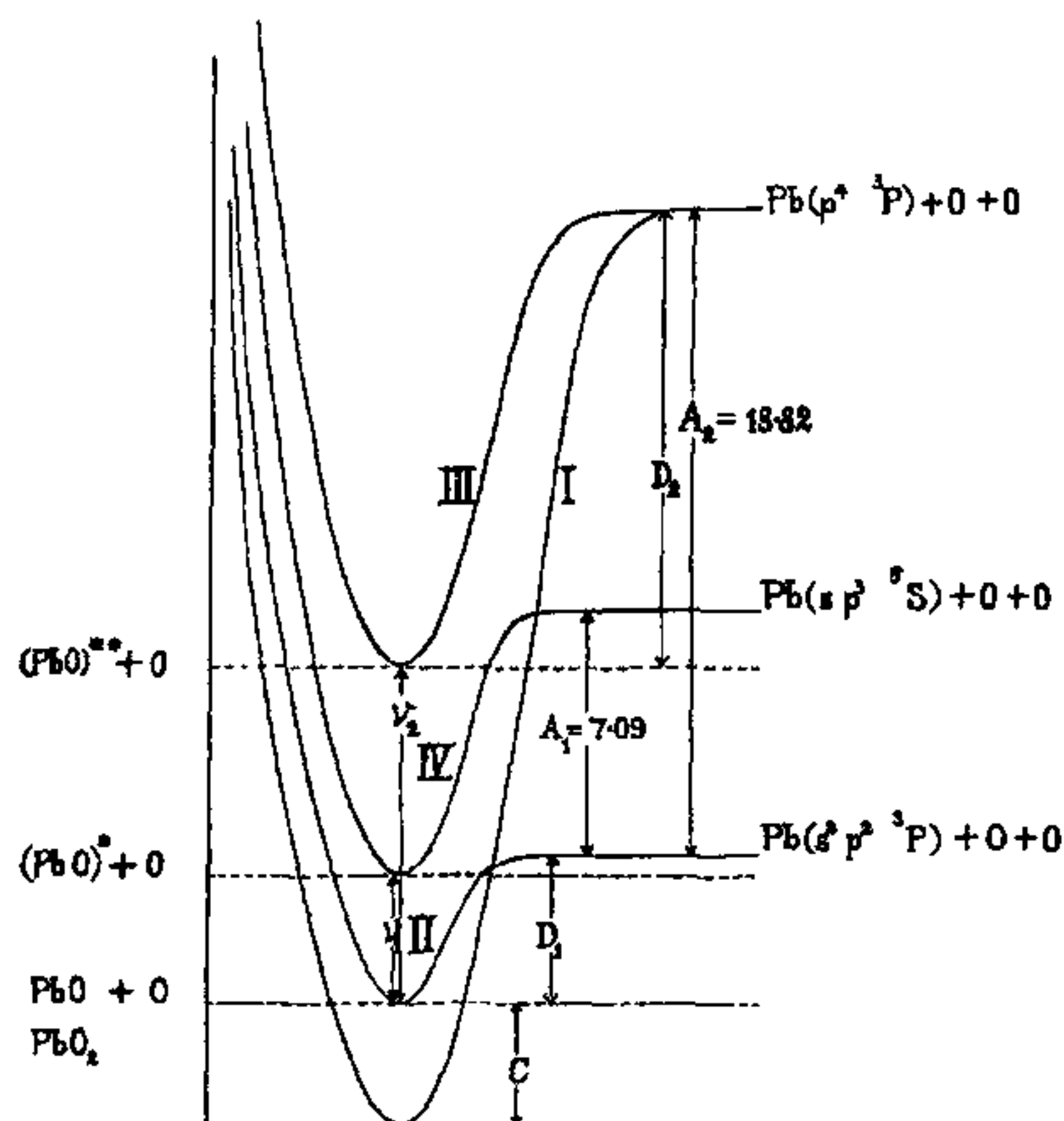
The carbon atom, *e.g.*, in its ground level $s^2 p^2 {}^3P$ is able to form a linkage with one O atom only, since the complete group of two s-electrons is chemically inert and acts repulsively; a second O atom cannot be linked from the ground level. Therefore already other authors, *e.g.*, Mecke (*Zs. f. phys. Chem. B.* 7, 108, 1930) have tried to explain the linkage of CO_2 by assuming an excited C atom in the $s p^3 {}^5S$ state. In a recent paper (*Zs. f. Phys.*, in press) we could show that apparently an s-electron does not undergo a linkage with the p-electrons of a negative partner. So, for the second linkage of CO_2 we have to assume a C atom excited to the $p^4 {}^3P$ state. This is all the more so because it is known from the chemical behaviour as well as from the infra red spectra that there is no difference between the linkages of the two O atoms.

In the case of the homologous molecule PbO we are in a position to prove this also from band spectrum data.

The thermochemical data are not fully known, especially our knowledge of the specific heat and of the heat of evaporation is insufficient. So the values of the molar heats of PbO and PbO_2 are graphically extrapolated in the range where no measurements are available, the values of the heat of evaporation are calculated by means of Trouton's Rule (Grüneisen's modification). That the data employed in the calculation are fairly correct can be taken from the fact that we found the heat of dissociation of PbO to be $D_1 = 4.38$ volts, in best accord with the spectroscopical value $D_1 = 4.27$ volts. Some uncertainty arises only in the case of the dissociation energy of PbO_2 , where we had to estimate even the melting and boiling temperatures; but this does not matter because we shall soon see how to get rid of this uncertainty. We obtain provisionally



Considering the system $\text{Pb} + \text{O} + \text{O}$, we have found now three energy levels, the lowest one being that of PbO_2 , another one of the system $\text{PbO} + \text{O}$, 2.05 volts higher, and a third one of the system of the separated atoms $\text{Pb} + \text{O} + \text{O}$, 6.43 volts above the lowest, each consisting of atoms and molecules in their respective ground states. The terms $s p^3 {}^5\text{S}$ and $p^4 {}^3\text{P}$ of Pb require an energy of excitation of $A_1 = 7.09$ and $A_2 = 18.82$ volts respectively. Thus we get



at curves I and II of the figure. Knowing as mentioned above that the amounts of energy by which the first and second O atoms are bound are equal, we have to halve the total dissociation energy of the PbO_2 bond (25.25 volts) to get the minimum point of curve III at $\nu_2 = 10.58$ volts above the minimum point of II. This is the energy level of the system $\text{PbO} + \text{O}$, PbO being in that excited state in which it is able to accept the second O atom, and dissociating in $\text{Pb}(p^4 {}^3\text{P}) + \text{O}$.

These calculations, if correct, enable us to predict the energy level of the PbO molecule derivable from the Pb in the $s p^3 {}^5\text{S}$ state. The amounts of energy wanted for the excitation of the first and second s-electrons though of course different in Pb and PbO will be in almost the same ratio in either case. We divide ν_2 in the proportion $A_1 : A_2$ and find the minimum point of the predicted curve IV at $\nu_1 = 3.99$ volts above the ground level of the PbO molecule. The dissociation energy of the molecule in this state results to about 7.5 volts.

This method of calculation applies to any molecule of this kind. We selected PbO because the predicted energy level is well known from band spectra proving the soundness of the fundamental idea. The D-bands of PbO are a ${}^1\Sigma - {}^1\Sigma$ transition, the upper state lying at 3.71 volts with an energy of dissociation of 8.24 volts. Considering the uncertainty of the thermochemical data employed these figures are in full agreement with the predicted ones. Besides another electronic level (III) of the PbO molecule is predicted, arising from the $\text{Pb}(p^4 {}^3\text{P})$ state with the electronic transition ν_2 from the ground level and the dissociation energy $D_2 = A_2 + D_1 - \nu_2 = \nu_2 + C$.

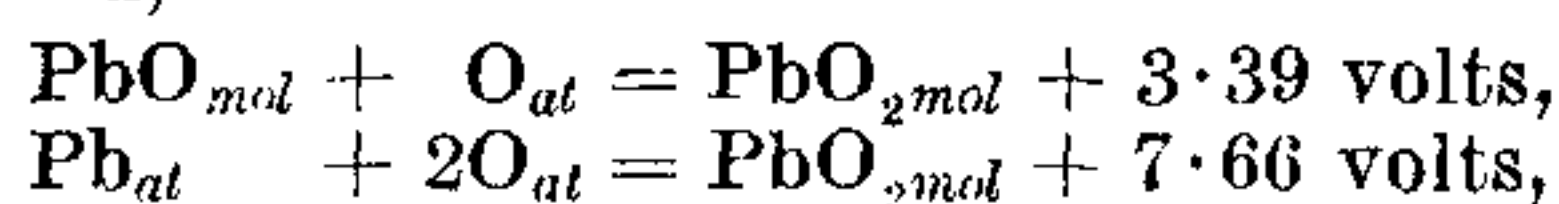
Putting the results in the form of equations we get,

$$\nu_1 = \frac{A_1}{2} + \frac{A_1}{2A_2} (D_1 - C) \quad (1)$$

$$\nu_2 = \frac{1}{2}(A_2 + D_1 - C) \quad (2)$$

$$D_2 = \frac{1}{2}(A_2 + D_1 + C) \quad (3)$$

Now by means of equation (1) we can rid ourselves of the uncertainty in the thermochemical calculations and in the reverse find better values for the thermochemical data. Using the spectroscopical values $\nu_1 = 3.71$ volts, $D_1 = 4.27$ volts, which are more exact, and introducing them into (1), we find,



Total heat of dissociation of $\text{PbO}_2 = 26.48$ volts,

$$\begin{aligned} \nu_2 &= 9.85 \text{ volts,} \\ D_2 &= 13.24 \text{ volts.} \end{aligned}$$

As to the energy of the bonds of the different electronic groups another interesting result can be obtained. We have seen now that the upper state of the D-bands of PbO comes from the $\text{Pb}(s p^3 {}^5\text{S})$ a result already got in another way in the paper mentioned above. The excitation of the molecule corresponding to the D-bands means the transition of an electron from $p\sigma(s)$ in the lower state to $f\sigma(p)$ in the higher one. Either group is a so-called promoted group, i.e., it loses energy when the distance of the nuclei decreases. The energy of excitation ${}^5\text{S} - {}^3\text{P}$ of the Pb atom is higher than the corresponding energy ${}^1\Sigma - {}^1\Sigma$ of the PbO molecule. So the dissociation energy being higher in the upper level than in the ground-most one we can say that the promotion of the $f\sigma(p)$ group cannot have started at the nuclear distance of the PbO molecule to any considerable extent or at least is much less

than that of the $p\sigma(s)$ group, for otherwise the energy of dissociation would decrease with excitation.

Thus it is evident that there exists a near connection between the energy states of a diatomic molecule and a triatomic one

derived from it. It is also shown that atoms of the fourth family, *e.g.*, C, really undergo a tetravalent linkage from the $p^4 \text{ } ^3P$ term. This has to be considered in many questions of thermo-chemistry. A full report will be given elsewhere.

Influence of Wall Effect on the Nature of Coagulation Process.

By Dr. B. N. Desai, M.Sc., Ph.D.,

Wilson College, Bombay.

IT has been realised by investigators in colloid chemistry that the walls of the containing vessel may affect the rate of coagulation. Desai (*Trans. Faraday Soc.*, **24**, 181, 1928; Patel and Desai, *ibid.*, **26**, 128, 1930; Desai, *Kolloidchem. Beihefte*, **26**, 357, 1928; cf. Freundlich, *Colloid and Capillary Chemistry—Eng. Translation—1926*, p. 417) has discussed in detail the defects in the various methods used for following the course of coagulation which might be responsible for the observance or non-observance of the S-shaped coagulation velocity (C.V.) curves and the auto-catalytic nature of the coagulation process. In discussing the ultra-microscopic method it has been pointed out that the walls of the cell containing the colloid might have also some effect on the course of the coagulation reaction and that there is a possibility of greater percentage error with dilute sols—which alone can be used with this method—than with concentrated ones owing to the wall effect. In a concentrated sol the number of colloidal particles being comparatively larger than in a dilute sol, the effect of the walls in acting as centres for coalescence will be negligible.

In a recent paper S. S. Joshi and V. L. Narayan (Special Number of the *Journal of the Indian Chemical Society*, 1933, p. 41) have studied in detail the influence of wall area in the coagulation of colloidal solutions of MnO_2 , Sb_2S_3 and (+ively charged) Fe_2O_3 . The concentration of the disperse phase in the colloidal solutions tried by them is not very high. They have observed that the rate of coagulation is markedly increased in all cases when the wall area of the coagulating system is increased by introducing glass beads. They also find that when the same number of beads and the containing walls are paraffined, the coagulation is sensibly retarded in all cases. In the light of their

results they consider unlikely that the increase in the rate of coagulation, under wall effect alone, can convert a 'slow' into a 'rapid' coagulation. They conclude that auto-catalysis cannot be considered as a general characteristic of coagulation as has been supposed by some workers, but that it is a secondary process which adds to the main course of coagulation under certain conditions.

It will not be out of place to consider in some detail the results of Joshi and Narayan in this letter as they have an important bearing on the theory of slow coagulation proposed by Freundlich (*loc. cit.*, pp. 431-447). As shown by electrosmotic, cataphoretic and stream-potentials measurements, the wall-layer of glass in contact with water becomes negatively charged. The nature of this charge will be modified considerably in the presence of electrolytes as well as when the glass surface is paraffined. It is, therefore, certain that the glass surface will help or retard the coagulation according to the nature of the charge on it and on the colloidal particles. Moreover glass walls themselves, whether paraffined or not and whether charged or uncharged, will act as centres for coalescence. In view of these considerations, it is not justifiable to say that the results of Joshi and Narayan support the conclusion that the nature of coagulation process is not intrinsically auto-catalytic.

On the other hand, their results can well be utilized to show that the nature of coagulation process is auto-catalytic. For as shown by them the walls of the containing vessel (unparaffined) make the S-shape of the C. V. curves less marked and it is quite likely that non-observance of auto-catalysis by some workers might be to a certain extent due to this effect. As shown by Desai (*loc. cit.*) the appearance of the