

formula is to be modified for complex substances such as liquids and solids. That solids have surface tension has now been pretty well established. In the case of adsorption of gases the adsorbed molecules are held to the surface of the adsorbent by cohesive forces. Now it has been observed that the same adsorbent may adsorb varying amounts of adsorbent, when subjected to different treatment. Activation of charcoal is a familiar instance. It is supposed that the specific surface increases with activation. Now if the total surface energy be the same then the increase of surface would be associated with the decrease of surface energy per unit surface and this would lead to a corresponding decrease of adsorption per unit area. This is not actually the case. The total adsorption increases and if the adsorption per unit surface is the same, this would mean constancy of surface energy. Thus for solids it is preferable to study surface tension by considering the surface density of molecules distributed over surface, the surface layer being one or several molecules thick and this  $\rho$  in the expression (1) should be replaced by  $1/\Omega$ ,  $\Omega$  being the available surface.

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<sup>1</sup> Sibaiya, *Curr. Sci.*, 1935, 3, 418.

<sup>2</sup> Cantor, *Wied. Ann.*, 1892, 47, 421; *Handbuch der Physik*, 7, 394.

<sup>3</sup> Lennard-Jones, *Proc. Roy. Soc., A*, 1928, 121, 247; *Fowler's Statistical Mechanics*, chap. X.

<sup>4</sup> Eisenschitz and London, *Z. Phys.*, 1930, 60, 520; London, *Z. F. Phys. Chem., B*, 1931, 2, 221.

<sup>5</sup> Gyemant, *Handbuch d. Phys.*, 7, 346.

<sup>6</sup> Lennard-Jones, *Proc. Phys. Soc.*, 1931, 43, 461.

<sup>7</sup> Polanyi and London, *Naturwiss.*, 1930, 18, 1099.

<sup>8</sup> Ganguli, *Koll. Zeit.* (In the press); Burrage, *Farad. Soc. Trans.*, 29, 445; Besl and Reinhardt, *Z. Phys. Chem.*, 1933, 166A, 81.

### Colloidalisation and Cold-Working of Metals.

THE subject of the magnetic properties of non-ferromagnetic metals has attained much interest recently in view of the work of Pauli, Sommerfeld and others on the theory of the metallic state.<sup>1</sup> The simplest picture of the metal that will suit our purpose consists of a lattice of metallic ions, the remaining electrons in each atom being associated with two or more nuclei and

considered as free or partly bound in accordance with their relative energy values. The susceptibility of the metal is to be considered as the sum of the susceptibilities of the ions and of the remaining or valency electrons of the individual atoms. The first part is a constant while the second is greatly influenced by the physical conditions. The large deviations in the values for metals obtained by different workers is to be attributed to the fact that their metals were not in the same state and hence the susceptibility of the valency electrons should have been greatly different.

The valency electrons may have large orbits as contemplated by Ehrenfest<sup>2</sup> for graphite and by Raman<sup>3</sup> for bismuth. Or they may be attached loosely to two close atoms, being considered as free or partly bound. On colloidalisation, the first type would give rise to decreased diamagnetism due to the fact that large orbits could not be possible at the surface. This conclusion has been experimentally established for graphite<sup>4</sup> and bismuth,<sup>5</sup> and in fact, in the case of graphite, Krishnan and Ganguli<sup>6</sup> have determined the direction of largest variation as the one parallel to the hexagonal axis.

In the case of good conductors, the state of affairs is different. The electrons on the surface of the atoms may be considered as free, the number of such electrons being of the same order as the number of atoms in the metal. Considered as free, the electrons possess the Pauli paramagnetism and if regarded as confined to a series of energy bands, they contribute a diamagnetic component.

Honda and Shimizu<sup>7</sup> have shown that cold-working in the case of copper and silver gives rise to increased diamagnetism. They have quantitatively accounted for this result as being due (1) to the decrease in paramagnetic component due to the diminution of free electrons caused by the expansion on cold-working (for which there is ample evidence from X-ray data<sup>8</sup>) and (2) to the increase in the diamagnetic component due to the increased number of bound electrons. They explain that the lattice constant is a little greater in the surface layer than in the interior, the normal value for the metal being reached at some hundred layers below the surface. Thus colloidalisation should be accompanied by increased diamagnetism quite similar to what is obtained in the case of cold-working.

Attention has been drawn to this similarity in the case of tin by Honda and Shimizu.<sup>9</sup>

I have recently verified this result in the case of copper. Colloidalisation by condensed electric discharge in an inert organic liquid in the absence of air, gives rise to an increase in the diamagnetic susceptibility. The question of impurities affecting the measurements does not arise here since all the ordinary compounds of copper are paramagnetic or less diamagnetic than the metal. Here then we have a new kind of increased diamagnetism on colloidalisation.

I take this opportunity of drawing attention to a recent letter in these pages by Verma and Gupta.<sup>10</sup> They have once again drawn attention to the old question of impurities modifying the results. I shall content myself here by just mentioning that they have not been fair to the literature on the subject. It is enough if mention is made of the fact that the fundamental experiment which settled the decrease of diamagnetism on colloidalisation in the case of bismuth was the observed recovery of the value of 1.32 (the value for the mass metal) on melting and cooling of a sample of the colloidal bismuth. In the rather profuse literature they have cited, they have omitted to quote the one paper<sup>5</sup> which outlined this conclusive experiment.

Full details will appear shortly elsewhere.

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<sup>1</sup> For a brief summary see Stoner, *Magnetism and Matter*, chapter XIV.

<sup>2</sup> *Physica*, 1929, 5, 388.

<sup>3</sup> *Nature*, 1929, 123, 945.

<sup>4</sup> *Ind. Jour. Phys.*, 1929, 4, 139; 1930, 5, 559; 1931, 6, 241.

<sup>5</sup> *Ind. Jour. Phys.*, 1932, 7, 35.

<sup>6</sup> *Curr. Sci.*, 1935, 3, 472.

<sup>7</sup> *Nature*, 1933, 132, 565.

<sup>8</sup> *Phil. Mag.*, 1934, 18, 495.

<sup>9</sup> *Nature*, 1935, 135, 108.

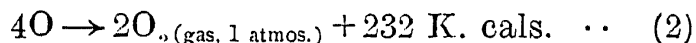
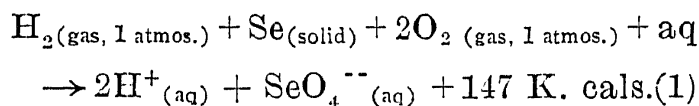
<sup>10</sup> *Curr. Sci.*, 1935, 3, 611.

#### A Note on the Bond Energies from Raman Frequencies and Thermochemical Data.

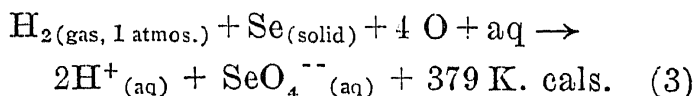
GANESHAN<sup>1</sup> has measured the Raman frequencies corresponding to the Se=O and S=O bonds. From the data collected by him, it is clear that there is a general agreement between the bond energy values got from

light scattering and those obtained from thermochemical data. A closer examination, however, reveals an appreciable discrepancy between the values of the heats of dissociation calculated from the Raman frequencies and those obtained from the thermochemical data relating to the ions. The present note deals with the significance of this disagreement.

It is to be noted that the heats of formation of the ions  $\text{SeO}_4^{--}$ ,  $\text{SeO}_3^{--}$ ,  $\text{SO}_4^{--}$  and  $\text{SO}_3^{--}$ , as given in the *International Critical Tables* (5, p. 178) are only relative in so far as they are calculated by arbitrarily assuming that the heat of formation of  $\text{H}^+_{(\text{aq})}$  from  $\text{H}_2$  (in its standard state) is zero. In view of this fact, the values calculated by Ganeshan are to be interpreted as follows:

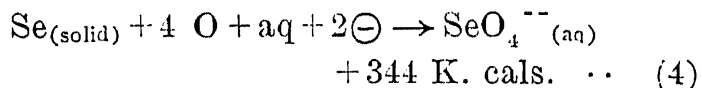


Combining equations (1) and (2), one gets

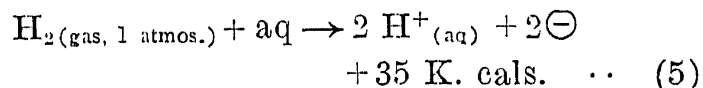


Since the heat of formation of  $\text{H}^+_{(\text{aq})}$  is not known, that of  $\text{SeO}_4^{--}_{(\text{aq})}$  cannot be calculated. Furthermore, the heat of reaction as given in equation (3) does not give the absolute value of the heat of formation of  $\text{SeO}_4^{--}$ , so that one cannot expect it to agree with the value got from the Raman frequency of the Se=O bond.

The question then arises as to whether the Raman frequency gives an idea of the absolute heat of formation of  $\text{SeO}_4^{--}$  ion in solution. If this is true, one can put



Combining equations (3) and (4), one gets,



It is also possible to calculate the heat of reaction in equation (5) by knowing the Raman frequencies of  $\text{SeO}_3^{--}$ ,  $\text{SO}_4^{--}$  and  $\text{SO}_3^{--}$ . Table I gives the values so obtained.

The large variance in the values for the heat of formation of  $\text{H}^+_{(\text{aq})}$  indicates that the Raman frequencies enable one to calculate only the heat of formation of molecules but not of ions in solution.