

LETTERS TO THE EDITORS

The Editors do not hold themselves responsible for opinions expressed by their correspondents. No notice is taken of anonymous communications.

Electron Spin Resonance of Coals : Saturation Effect

IN an investigation into the electron spin resonance of coal, I found a saturation effect depending on the percentage of carbon contained in the coal. The samples, all of them vitrinites, were examined in air; the frequency at which the measurements were made was 9,000 Mc./s.

It was found that in those cases where the saturation could well be measured the saturation factor Z showed good agreement with the theoretical expectation given by

$$Z = (1 + \frac{1}{2}\gamma^2 H_1^2 T_1 T_2)^{-1}$$

In this formula γ is the gyromagnetic ratio, H_1 the amplitude of the alternating magnetic field, T_1 the spin-lattice relaxation time and T_2 the spin-spin relaxation time. As Z , H_1 and T_2 could be experimentally determined, T_1 could be calculated.

Instead of T_1 Fig. 1 gives the variation of $P(Z=0.5)$ as a function of the rank. We define $P(Z=0.5)$ as that amount of energy dissipated in one gram of coal, for which the saturation factor Z becomes equal to 0.5. In some cases, for example, when measuring the number of free radicals, this quantity may have a more direct significance to the experimental investigator than the value of T_1 .

A variation similar to that in Fig. 1 may probably be expected if for some sugar chars $P(Z=0.5)$ is plotted as a function of the carbonization temperature¹.

From Fig. 1 it is seen that at carbon percentages less than 88 the value of $P(Z=0.5)$ is very low, so

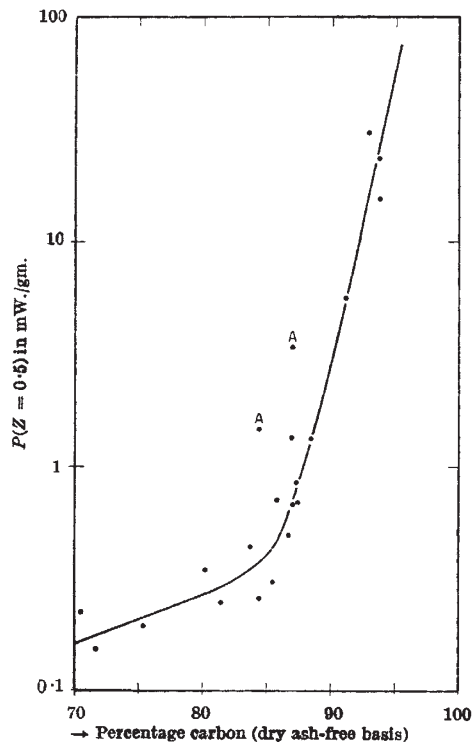


Fig. 1

that in determining the number of free radicals in this range there is a risk of measuring them in a saturated state and hence of finding a number which is lower than the actual one.

At carbon percentages greater than 86 the value of $P(Z=0.5)$ shows a rapid increase. Lacking an energy source of sufficient power, I have not been able to measure the saturation effect beyond 94 per cent carbon. That the value of $P(Z=0.5)$ in this range must be very high is corroborated by the facts that a $P(Z=0.5)$ -value of 1 mW./gm., for the coal under consideration corresponds to $T_1 \approx 4 \times 10^{-5}$ sec., and that Garif'yanov and Kozyrev² measured $T_1 = 12 \times 10^{-8}$ sec. for an anthracite.

I would also direct attention to the influence of ash content. In two cases measurements were made on samples of low and high ash contents (the latter samples are indicated by A in Fig. 1). It is seen that the presence of ash causes a rise of $P(Z=0.5)$. At the same time T_1 decreases, which suggests an increase in the exchange between the unpaired electrons and the surroundings. In both cases the samples of high ash-content proved to contain more free radicals than the practically ash-free samples, which seems to indicate that, at least in the two cases considered, the ash contains paramagnetic components.

J. SMIDT

Central Laboratory,
Staatsmijnen in Limburg,
Geleen, The Netherlands.
Nov. 19.

¹ Uebersfeld, J., and Erb, E., *C.R. Acad. Sci., Paris*, **243**, 2043 (1956).

² Garif'yanov, N. S., and Kozyrev, B. M., *Zh. Eksper. Teor. Fiz.*, **30**, 1160 (1956).

Dispersion Energies in Porous Sorbents

De Boer and Custers¹, by an integration process, approximated to the energy of interaction by dispersion forces between a molecule and several types of cavity. On a plane surface containing N atoms of substrate per cm.² the interaction energy is near to

$$E_1 = -\frac{\pi NA}{6} \times \frac{1}{r^3} \quad (1)$$

if the interaction energy between an isolated sorbate molecule and the nearest atom of sorbent is given by $-A/r^6$. A is a constant given approximately by the London theory of dispersion forces². Then, in turn, in a hemispherical pocket, at the bottom of a very long cylindrical capillary with a hemispherical end, and in an isolated spherical cavity, all of radius r and just large enough to contain the molecules, the energies of interaction are respectively $E_2 = 4E_1$, $E_3 = 6.36E_1$ and $E_4 = 8E_1$.

This calculation indicates that very large maximum enhancements of sorption energies could be expected in suitable capillaries. For two plane parallel surfaces r apart, $E_5 = 2E_1$. Thus, in slit-shaped cavities such as could occur with graphite, the ratio between initial and limiting heats of sorption may approach two. Such a ratio has indeed been observed, and the above explanation of it has been suggested³. However, with highly porous sorbents one may easily exaggerate the enhancement of dispersion forces due to environment, and I wish to subject the idea of this enhancement to a more critical examination.

In the first instance the perfect fit of a sorbate molecule into the pocket (energy = E_2), channel