

If a solvent such as isopropyl alcohol is used instead of the above, one gets only intensification of peaks even for anion-nickel ratios greater than two. This holds for both chloride and thiocyanate. It is interesting that study of continuous variations of these solutions shows a maximum apparent complexing of four anions per nickel⁷. This apparent limit might be due to problems of replacing further solvent groups, rather than an indicator of pure 4-co-ordination, as the alcohol is a stronger electron donor than acetone, and tends to maintain the higher co-ordination number of cations⁸ (with iodide, co-ordination to six groups per nickel can be seen). It might be added that Ni(II) in fused nitrate salt melts is green, and that a blue colour develops on addition of chloride, with a spectrum similar to that of our blue acetone solutions (D. Gruen, private communication). Small amounts of nickel incorporated into solid Cs_2ZnCl_4 (tetrahedral ZnCl_4^{2-}) also show the same blue spectrum.

It is therefore suggested that the blue compounds studied by Lifschitz, Bos and Dijkema² were in fact tetrahedral, as is also the chloride (in excess chloride) in acetone and tributyl phosphate. The blue colour arises mainly by disappearance of the 410-m μ peak, as would be predicted from Low's⁴ analysis of the levels for the Ni(II) ion in the octahedral crystalline field. One may venture to state the following generalization: paramagnetic nickelous compounds which are the normal green colour, or the spectra of which show the equivalent of the 410-m μ absorption peak of the green form, are to be presumed to be 6-co-ordinate, or at least to possess the electronic structure characteristic of the 6-co-ordinate state. Paramagnetic compounds of Ni(II) which fail to show this absorption peak (and which may be blue, if the colour is not masked by the ligand) are presumably tetrahedral, or have the equivalent electronic structure. Diamagnetic compounds have, of course, the square planar form.

This work was performed under the auspices of the U.S. Atomic Energy Commission.

LEONARD I. KATZIN

Chemistry Division,
Argonne National Laboratory,
Lemont, Illinois.
Sept. 5.

¹ Pauling, L., "Nature of the Chemical Bond", 2nd ed. (Cornell University Press, 1949).

² Lifschitz, I., Bos, J. G., and Dijkema, K. M., *Z. anorg. u. allgem. Chem.*, **242**, 97 (1939).

³ Maki, G., *J. Chem. Phys.*, **28**, 651 (1958); **29**, 162 (1958).

⁴ Low, W., *Ann. N.Y. Acad. Sci.*, **72**, 69 (1958).

⁵ Gorter, C. J., *Phys. Rev.*, **42**, 437 (1932).

⁶ Kittel, C., and Luttinger, J. M., *Phys. Rev.*, **73**, 162 (1948).

⁷ Katzin, L. I., and Gebert, E., Proc. All-day Conf., Chicago Section, Amer. Chem. Soc., November 23, 1951.

⁸ Katzin, L. I., *J. Inorg. Nucl. Chem.*, **4**, 187 (1957).

function of the hydrogen pressure and that the addition of small amounts of steam to the atmosphere of hydrogen has no apparent effect on the rate of formation of methane. It is suggested that the mechanism of methane formation is the same. The rate of formation of methane, for the same carbon, prepared at 950° C., with 30 atm. of steam at 870° C., is 16×10^{-5} gm.mol./min./gm. carbon, and with hydrogen under the same conditions is 10×10^{-5} gm.mol./min./gm. carbon. The rate varies with the temperature of preparation of the carbon and lower-temperature carbons are more reactive, reaching a maximum reactivity to hydrogen when prepared at about 750° C.

Similar results were obtained by Goring *et al.*³ in the gasification of 'Disco' char with a steam-hydrogen mixture at 870° C., their results showing that there is no significant change in the rate of formation of methane at a given temperature and pressure when the reactant gases are mixtures of steam and hydrogen in the ratios 50/50, 75/25 and 90/10. Their gasification rate at 870° C. and 30 atm. pressure was approximately 33×10^{-5} gm.mol./min./gm. carbon, and later experiments in the same apparatus with similar char⁴, using hydrogen only as the reactant gas, gave a rate of 40×10^{-5} gm.mol./min./gm. carbon. Wood charcoal, prepared at 870° C. from *Eucalyptus marginata*, when made to react with hydrogen under the same conditions of temperature and pressure, gave² a rate of formation of methane of approximately 45×10^{-5} gm. mol./min./gm. carbon.

It has been suggested¹ that the carbon-steam reaction is controlled by oxygen groups attached to the carbon and that the methane produced is formed by reaction of steam with adsorbed hydrogen, liberating methane and carbon monoxide. The formation of methane by reaction of hydrogen with carbon is believed to be controlled by oxygen groups, such as chromene or benzpyran, in the carbon structure², and it now appears that these may be effective in controlling methane production in both the carbon-steam and carbon-hydrogen reactions.

The formation of methane during the carbon-steam reaction is important technically since it results in a reduced heat requirement for the gasification of carbon with steam due to the exothermic nature of the reaction producing methane.

J. D. BLACKWOOD

Division of Industrial Chemistry,
Commonwealth Scientific and
Industrial Research Organization,
Melbourne.
Sept. 4.

¹ Blackwood, J. D., and McGrory, F., *Aust. J. Chem.*, **11**, 16 (1958).

² Blackwood, J. D., *Aust. J. Chem.* (in the press).

³ Goring, G. E., Curran, G. P., Tarbox, R. P., and Gorin, E., Pittsburgh Consolidated Coal Co. Library (Pennsylvania, 1951).

⁴ Zielke, C. W., and Gorin, E., *Indust. Eng. Chem.*, **47**, 820 (1955).

Production of Methane from Carbon

THE recent work of Blackwood and McGrory¹ has shown that methane is formed when carbon, in the form of coconut char, is allowed to react with steam under pressure. The rate of formation of methane is a linear function of the steam pressure and appeared to be independent of the partial pressure of hydrogen when the latter is small. A similar study² of the reaction of hydrogen and carbon under pressure at temperatures of 650–950° C. has shown that the rate of formation of methane is a linear

Paper as a Carrier of Chromium Sesquioxide

CHROMIUM sesquioxide (Cr_2O_3) is widely used for estimating feed digestibility¹ or faeces output² by ruminants, but such estimates may be subject to considerable errors because the concentration of this marker in faeces normally shows considerable diurnal variations even after prolonged regular administration. These variations are particularly obtrusive with grazing animals where the chromium sesquioxide, in