the carbon monoxide content of the gas was negligible, so that little positive evidence was forthcoming in favour of the theory advanced by Bangham and Thring^{2,3}, according to which about half the release of energy in fuel-bed combustion takes place in the voids between the fuel particles.

Quite a different state of affairs was revealed, however, when an attempt was made to 'freeze' the gas mixture by the aid of chemical inhibitors. (Other workers have resorted either to the use of low gas pressures—thus minimizing the probability of collision of the surface products with other molecules in the region of the reaction zone—or alternatively to the use of normal pressures and low fuel-surface temperatures⁴.) The use of carbon tetrachloride and phosphorous oxychloride was suggested by the work of Dufraisse and his collaborators^{5,6}. The effect of chlorine has also been examined. When small quantities of these materials were included in the air-stream (which was dried over sulphuric acid and magnesium perchlorate) greatly increased quantities of carbon monoxide were found in the samples taken about 1 mm. from the carbon wall. The accompanying table demonstrates this and gives in each case representative observations after reaching a steady state.

Inhibitor	% by volume of inhibitor in air-stream	Gas analyses (%) CO ₂ O ₂ CO	Temp. at carbon wall 1 cm. upstream of sampling point (°C.)
Cl ₂	0	17.5 2.5 0.6	775
	1.0	10.1 2.4 14.6	770
	1.0	9.6 1.2 15.5	770
CCl ₄	0	14.6 5.8 0.7	815
	1.8	8.8 4.4 14.3	800
	1.8	8.2 1.9 16.1	795
POCl ₃	0	16.3 4.1 0.6	805
	0.9	5.0 2.6 21.1	785
	0.9	5.5 2.9 22.3	785

Note.—The CO₂ figures with the inhibitors present include small amounts (< 1 per cent) of chlorine.

While it must remain for further experiments to establish whether or not these added materials also influence the surface reaction (by causing a large increase in the ratio of carbon monoxide to carbon dioxide in the gases leaving the carbon surface), the above results by themselves indicate that they function very efficiently as inhibitors of the gas-phase reaction, since appreciable quantities of oxygen and carbon monoxide co-exist in the gas. Thus a supposed effect on the surface reaction only is insufficient to account for the results. (Unpublished experiments by K. D. Wadsworth have suggested that carbon tetrachloride has little effect on the time of ignition of coal surfaces as measured under standardized air-flow conditions.) The marked effect of the halogens and their compounds on the ignition temperature and oxidation of carbon monoxide (and other combustible gases) has been frequently demonstrated⁸. The suppression of the gas-phase oxidation recorded above is presumably effected by a reactive species removing an essential link in the chain mechanism mainly responsible for the oxidation.

These experiments therefore strongly suggest that: (a) very rapid quenching is of the first importance when a reliable analysis is required of a hot gas mixture containing carbon monoxide and oxygen; (b) the bulk of the energy discrepancy first recorded by Nicholls is due to deficiencies in the gas-sampling technique; (c) the high-temperature oxidation of carbonaceous fuels takes place by a mechanism in which the gas-phase oxidation of carbon monoxide plays a significant part.

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Resonance Energy of the Tetrachlorethylene Molecule

RECENTLY¹, it has been shown that the interpretation of a general potential function determining the modes of vibration for the C₂Cl₄ molecule supports the hypothesis of resonance among several electronic structures, leading for the C—C bond to a single-bond character of about 15 per cent. This result has been deduced partly from the fact that the C—C force constant lies between 8.0 and 8.5 × 10⁸ dynes/cm., as compared with 9.0 × 10⁸ dynes/cm. for ethylene, and partly from general considerations on the signs of the cross-terms. (From a private communication from Prof. C. Manneback, we adopt 9.0 instead of 9.3 as in our previous publications; in this case, the conclusions are even reinforced.) If so, following Pauling's arguments², the actual energy of formation of the molecule must be greater than the calculated value by a certain amount, called resonance energy of the system. The definite bond diagram used for our calculation corresponds to the classical distribution of valences and gives

$$\begin{aligned} \text{C}_2\text{Cl}_4(\text{gas}) &= 2 \text{C}(\text{gas}) + 4 \text{Cl}(\text{gas}) - E(\text{C}=\text{C}) - 4 E(\text{C}-\text{Cl}) \\ 2 \text{C}(\text{gas}) &= 2 \text{C}(\text{diamond}) + 2 L_c \\ \text{C}_2\text{Cl}_4(\text{gas}) &= 2 \text{C}(\text{diamond}) + 4 \text{Cl}(\text{gas}) - Q_{\text{calc}}. \end{aligned}$$

It is to be noted that the value $Q_{\text{calc.}} = E(\text{C}=\text{C}) + 4 E(\text{C}-\text{Cl}) - 2 L_c$ is not influenced by the not yet definitely established value of L_c . According to Pauling², the C—C bond energy is 100 kcal./mole, the C—Cl bond energy is 66.5 kcal./mole and L_c is 124.3 kcal./mole. Hence the heat of formation $Q_{\text{calc.}}$ is 117.4 kcal./mole.

The effective heat of formation $Q_{\text{obs.}}$ of the tetrachlorethylene gas molecule remains now to be determined from the heat of combustion and the heats of formation of the products of combustion.

Following the experimental results obtained by Thomsen and adopted by Bichowsky and Rossini³, we obtain $Q_{\text{obs.}} = 108.3$ kcal./mole. (In a private communication, Dr. Rossini has given us arguments against the alternative determination of the heat of combustion of C₂Cl₄ by Berthelot⁴. It leads to a value in the range of 150 kcal./mole for $Q_{\text{obs.}}$, which is considerably different from that obtained from Thomsen's data. Nevertheless, we cannot consider this value as completely ruled out.) In spite of the slight negative discrepancy between $Q_{\text{calc.}}$ and $Q_{\text{obs.}}$ (—9.1 kcal./mole) the idea of resonance must not necessarily be abandoned, as this discrepancy lies within the limits of the probable errors in the experiments.

In any event, new and accurate measurements for the chlorinated hydrocarbons are of great importance for the further development of the question of determining the resonance energy by the Pauling method.

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Saturated Adsorbed Films and the Structure of Deeply Super-cooled Water

DR. F. C. FRANK, in a recent note¹, has directed attention to the work of Rau² who, by a process of repeated freezing and thawing which 'sterilized' the nuclei of solidification, succeeded in super-cooling water to —72°C., at which temperature it invariably froze. The water was in the form of droplets (up to a few millimetres in diameter) supported on a highly polished surface of chromium or nickel. The system being enclosed, so that the cooled metal plate was its coldest part, it is certain that the vapour in contact with its surface was saturated.

The point of special interest to which Frank directs attention is that the droplets flattened below —50° and spread to a film at —70°C. In other words, the equilibrium contact angle decreases markedly in this region.

The purpose of this note is to emphasize that these facts as stated do not imply that the surface tension of water decreases with fall of temperature in this region¹. What the contact angle measures is not the surface tension of the liquid, nor yet the wetting free-energy, but the degree of incongruity between the molecular patterns of the saturated adsorbed film on one hand and of the liquid water surface on the other³. Adsorption experiments have made it clear that in the presence of saturated water vapour the metal surfaces would be coated with adsorbed films of water, almost certainly of more than uni-molecular thickness. These films are none the less significant because they are invisible.

The molecular configuration in films which (like that of water on charcoal) may be three or four molecules in thickness and yet not render the surface completely *wettable* has been a preoccupation of mine for a number of years. It may be noted, in this connexion, that the 'inverted' configuration—postulated by Frank¹ for the supercooled water and characterized by formation of small closed groups which behave kinetically as complex molecules between which only the relatively weak van der Waals forces are acting—is similar to that assigned by me to the films of lower alcohols on charcoal on the basis of the measured properties of the latter⁴.

The correct interpretation to be placed upon Rau's observations is, therefore, that as water is cooled below —50°C., its molecular pattern and especially, in all probability, that of its surface layers, approaches more and more closely that characteristic of the films formed by adsorption of water vapour on the metal surfaces.

Whereas, with water (and the alcohols), hydrogen bonds beyond doubt play an important part in determining the configuration of the 'inverted' groups, it must be strongly emphasized that their presence is in no way essential for the formation of molecularly thick films in which the molecular pattern differs from that of the normal liquid. Thus, by exposing plates of mica to jets of the supersaturated vapours, it was found possible, both with polar and non-polar liquids, to build up films of visible thickness upon which drops of the normal liquids would not spread⁵. The contact angles were therefore finite, indicating a configurational difference between drops and films.

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