corresponding heat of formation is known. Recent work (Kemball, C., Wyn Roberts, M., and Saleh, J. M., unpublished results) on the sulphiding of metals has suggested that the binding energy of sulphur to nickel at — 80° C. is somewhat greater than the corresponding heat of hydrogen chemisorption ($\sim$ 35 kcal. mole^{-1}). If the chemisorbed layer similates nickel sulphide we would expect, on the above hypothesis, a value of about 50 kcal. mole^{-1} for the heat of sulphur chemisorption since the heat of formation of nickel sulphide is — 17·5 kcal. mole^{-1}.

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[1] Fahrenfort, J., van Reijen, L. L., and Sachtler, W. M. H., "The Mechanism of Heterogeneous Catalysis" (Elsevier, 1960).
[2] Schuit, G. C. A., van Reijen, L. L., and Sachtler, W. M. H. (preprint, International Conference on Catalysis, Paris, 1960).
[3] Brennan, D., Hayward, D. O., and Trapnell, B. M. W., *Proc. Roy. Soc.*, A, **256**, 81 (1960).
[4] Beeck, O., Cole, W. A., and Wheeler, A., *Disc. Farad. Soc.*, No. 8, 315 (1950).
[5] Rudham, R., and Stone, F. S., *Trans. Farad. Soc.*, **54**, 420 (1960).

Heat of Adsorption of Hydrogen on Tungsten at Elevated Temperatures

Recent work[1],[2] has shown that when certain hydrides are adsorbed on tungsten filaments at low pressures, and temperatures around 1,750° K., part is apparently desorbed as a negative ion, and a residual hydrogen atom is left bound to the tungsten surface. At the low surface coverages prevailing under the conditions of experiment, the migration of these residual hydrogen atoms to adjacent sites is relatively slow, so that the process of desorption is energetically isolated from that giving rise to negative ions. The approximate strength of the tungsten–hydrogen bond formed in this process has been put at 73·5 kcal./mole (refs. 3 and 4) based on measurements at room temperature, and this value was used in deducing the mechanism outlined above, but as an order of magnitude only. Several results have now been obtained, and the argument may be inverted, to use these results in conjunction with established electron affinities and heats of atomization, to deduce the strength of the W—H bond at these elevated temperatures. Briefly, the apparent electron affinity, E', is related to the true electron affinity, E, the heat of atomization of the substrate, D, and the tungsten–hydrogen bond energy Q_r by the relation :

$$E' = E - D + Q_r$$

The values of E and D have been adjusted to a temperature of 1,750° K., the original data being taken from compilations[5],[6] except for the electron affinity of oxygen, taken from Branscomb and Smith[7]. The mean value of Q_r is 73 ± 1 kcal./mole, which is practically identical with the value at lower temperatures. If there was a loss of three translational degrees of freedom of the hydrogen atom in forming the W—H bond, the bond-energy would be expected

Table 1

Substrate	E'	E	D	Q_r
Hydrochloric acid	61	93	104	72
Hydrobromic acid	70	86	88	72
Water	−32	40	221	2 × 74

to rise by 5 kcal./mole at the higher limit of temperature, which is well outside the limits of experimental error, and the fact that the value is the same as, or slightly lower than, the room-temperature value suggests that there is a considerable degree of vibrational freedom in the adsorbed film. Two fully excited bending modes would lower the bond-energy to 72·0 kcal./mole from a value of 73·5 at room temperature, which is so close to the values obtained from the more reliable experiments with the halogen acids as to indicate that this is the true value at high temperatures. The differential heat of adsorption of molecular hydrogen on tungsten at limiting low surface coverage may readily be calculated to be 40 kcal./mole at 1,750° K., compared with 45 kcal. at room temperature.

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[1] Page, F. M., *Trans. Farad. Soc.* (in the press).
[2] Page, F. M., *Trans. Farad. Soc.* (in the press).
[3] Eley, *Disc. Farad. Soc.*, **8**, 34 (1950).
[4] Trapnell, "Chemisorption" (Butterworths, London, 1954).
[5] Pritchard, *Chem. Rev.*, **52**, 529 (1953).
[6] Cottrell, "The Strengths of Chemical Bonds" (Butterworths, London, 1959).
[7] Branscomb and Smith, *Phys. Rev.*, **98**, 1127 (1955).

Identification of Organic Compounds by Gas Chromatography

The identification of unknown compounds separated by gas chromatography is often effected by comparison of their retention values with those of known compounds together with infra-red spectrophotometry or mass spectrometry. For this purpose graphs are prepared of log r against boiling point or log r on one stationary phase against log r on another stationary phase, where r is the retention time, relative retention time or the retention volume. Both non-polar and polar stationary phases are used to indicate the nature of the unknown substance. Wehrli and Kovats[1] have shown a relation between the structure of the substance and its retention values on two such phases. Stationary phase liquids which can take part in electron donor–electron acceptor interactions have also been used by Langer et al.[2] and Janak and Hrivnac[3] to separate closely similar pairs of compounds. I have also found[4] three different stationary phases to be useful in identifying components of a brown coal tar.

A method has been developed for the identification of compounds by gas chromatography alone using three stationary phases ; one non-polar, one an electron donor and one an electron acceptor.

If r_1, r_2 and r_3 are the retention times (or volumes) of a substance on the three stationary phases 1, 2 and 3 under fixed conditions, we can define an 'affinity fraction' A of the substance for each phase. For phase 1 we have $A_1 = r_1/(r_1 + r_2 + r_3)$. This enables the data for a particular substance to be plotted as a point on a triangular graph.

The retention value r_b of a compound a on stationary phase b under a fixed set of conditions is proportional to $RT'/(\gamma^0_a p^0_a)$, where γ^0_a is the activity coefficient of a at infinite dilution in b and p^0_a is the vapour pressure of a at column temperature. For ideal solution behaviour r_b is governed by p^0_a. In non-ideal solution the value of γ^0_a is governed by the balance of interaction energies E between like