species and the meaning of temperature are in doubt, this definition can be put in ordinary thermodynamic terms. In thermal analysis change is so slow that temperature has its usual thermodynamic significance, so that $(\partial x/\partial T)_t$ is effectively zero in the experiments considered by MacCallum and Tanner.

R. A. W. Hill

Imperial Chemical Industries Ltd,
Research and Development Department,
Nobel Division,
Stevenston, Ayrshire.

Received April 27, 1970.

[1] MacCallum, J. R., and Tanner, J., *Nature*, **225**, 1127 (1970).
[2] Kissinger, H. E., *J. Res. Nat. Bur. Stand.*, **57**, 217 (1956).
[3] Russell, B., "Mathematics and the Metaphysicians" in *Mysticism and Logic* (George Allen and Unwin Ltd, London).

Rate of Hydrogen Dissociation at a Hot Tungsten Surface

THE atomization of molecular hydrogen at a hot tungsten surface has been studied extensively, some of the discussion being concerned with the correctness or otherwise of Langmuir's[1] early work. Moore and Unterwald[2] have summarized the various investigations up to 1964. In particular, it has often been stated that Langmuir's rates were "too low by factors which were all greater than 200", the quoted assertion being first made by Bryce[3] but often repeated since then (see for example refs. 3–6).

Langmuir used two techniques to measure the atomization rate. The first relates the rate of heat loss from a tungsten filament in a hydrogen atmosphere to the atomization rate, and is the more reliable[2]. In the second, the rate of removal of hydrogen by an "atom trap" is assumed to be equal to the rate of production of atoms by the hot filament. Until mass spectrometric methods were introduced, only the latter of these two techniques was used by other workers, and it is their results which are said to conflict with Langmuir's work. Recently, Roberts and Young[7], in studies of the kinetics of the interaction of hydrogen atoms with lead films, concluded that the incorporation of hydrogen into the lead lattice is activated, and is the slow step. At 78 K the rate of incorporation is a factor of nearly 100 slower than that observed with the film at 300 K. This result, like the earlier one of Anderson and Ritchie[6] with sodium films, implies that atom traps can vary in their trapping efficiency and in general are not expected to be perfect, still less to give rates much in excess[6] of those derived from heat loss measurements. We have accordingly examined the evidence for the alleged discrepancy (the factor of >200 by which Langmuir's rates were alleged to be too low) and conclude that it is without justification.

The most careful of the atom trap studies is that of Brennan and Fletcher[4], who obtained the following expression for the atomization rate n (atoms s^{-1} (cm^2 of W)$^{-1}$)

$$n = 18 \times 10^{24} \sqrt{p} \exp\ (-52{,}600/RT)$$

where p is the hydrogen pressure in torr.

Strictly speaking, this result holds only up to 1,400 K, and extrapolation to higher temperatures, necessary for comparison with Langmuir's heat loss data, would not be justified if the hydrogen pressure were less than 10^{-3} torr (ref. 4). Consider first Langmuir's heat loss data (over and above that caused by radiation and convection) for a hydrogen pressure of $1{\cdot}5 \times 10^{-2}$ torr and in the temperature range 1,800–2,900 K (ref. 1, page 435). The atomization rate can be computed from these data by equation 17 of ref. 1, page 427. For example, at 1,800 and 2,100 K, the rate is found to be $8{\cdot}4 \times 10^{17}$ and $5{\cdot}7 \times 10^{18}$ atoms s^{-1} (cm^2 of W)$^{-1}$ respectively, the requisite heats of dissociation being taken from Stull and Sinke[8]. The corresponding values from Brennan and Fletcher's equation (4) are $9{\cdot}1 \times 10^{17}$ and $7{\cdot}4 \times 10^{18}$ atoms s^{-1} (cm^2 of W)$^{-1}$, which are in good agreement with Langmuir's values. Even Bryce's data, which are considered to be in error from poor vacuum techniques, yield rates at 1,800 K and 2,100 K of $1{\cdot}0 \times 10^{18}$ and $6{\cdot}4 \times 10^{18}$ atoms s^{-1} (cm^2 of W)$^{-1}$, again in close agreement with Langmuir. The comparisons are almost as good if made at a hydrogen pressure of 1·1 torr, for which Langmuir also provides heat loss data.

Langmuir himself did not rate his second technique, in which atoms were trapped on a cooled glass surface, as highly as the first (ref. 1, page 452). Nevertheless, the results obtained from it compare favourably with those obtained by Bryce, who used the much more efficient MoO_3 trap. According to Langmuir's experiment 160 (ref. 1, page 541), the rate of hydrogen uptake on the cooled glass surface of the containing vessel was 1·4 mm^3 min^{-1} (cm^2 of W)$^{-1}$ at a hydrogen pressure of $1{\cdot}5 \times 10^{-2}$ torr and a tungsten temperature of 1,200 K. This corresponds to a rate of $1{\cdot}3 \times 10^{15}$ atoms s^{-1} (cm^2 of W)$^{-1}$ and compares favourably with the data of Bryce which yield a rate of $1{\cdot}9 \times 10^{15}$ atoms s^{-1} (cm^2 of W)$^{-1}$.

J. R. Anderson

CSIRO Division of Tribophysics,
University of Melbourne.

I. M. Ritchie*
M. W. Roberts

School of Chemistry,
University of Bradford, Bradford 7.

Received June 11, 1970.

* Present address: Clarendon Laboratory, University of Oxford.

[1] Langmuir, I., *J. Amer. Chem. Soc.*, **37**, 417 (1915).
[2] Moore, G. E., and Unterwald, F. C., *J. Chem. Phys.*, **40**, 2639 (1964).
[3] Bryce, G., *Proc. Camb. Phil. Soc.*, **32**, 648 (1936).
[4] Brennan, D., and Fletcher, P. C., *Proc. Roy. Soc.*, **A250**, 389 (1959).
[5] Brennan, D., *Adv. in Catalysis*, **15** (1964).
[6] Anderson, J. R., and Ritchie, J. M., *J. Phys. Chem.*, **70**, 368[illegible] (1966).
[7] Roberts, M. W., and Young, N. J., *Trans. Faraday Society* (in the press).
[8] Stull, D. R., and Sinke, G. C., *Adv. in Chem.*, **18**, 104 (1956).

NMR Relaxation in Heterogeneous Systems

THERE has recently been some discussion[1,2] of the difficulties of interpreting nuclear magnetic resonance line broadening in complex heterogeneous suspensions. The discussion has been concerned with hindered rotation of solvent species, and it has been confined to proton magnetic relaxation. We report here a study of the relaxation phenomenon in a well defined physicochemical system and contrast the results for proton and deuteron relaxation.

It is well known to NMR spectroscopists that particulate matter in a sample tube causes line broadening. The exchange of solvent species between the bulk phase average local magnetic field and that which exists near suspended matter is sufficient to cause broadening, and no reference to ordering or disordering of solvent is necessary to interpret it. The parameter necessary for interpretation in terms of disordering is the intra-term[3] for the spin-lattice relaxation time (T_1) which is obtained. only with great difficulty, from proton relaxation, not to mention line-width (or free induction decay), measurements.

A model system with quite well defined surface to volume ratios may be constructed by packing spheres of known radius in an NMR sample tube with the excess volume filled with water. Glass spheres with quite uniform diameters down to 15 μm are now commercially