Precise Measurement of Adsorption of Active Gases at Very Low Pressures by a Sensitive Pirani Gauge

In studies of adsorption, desorption and catalysis by solid surfaces, it is frequently desired to measure accurately the low pressure of active gases below 10^{-3} Torr. Although ionization gauges are used ordinarily for measuring pressure in this region, they are not always suitable for studying the adsorption of active gases in the very low pressure region, particularly in the case of closed systems. One of the reasons for this inapplicability is that the hot filament of the gauge gives a large pumping action and outgassing of the active gases.

In the course of adsorption measurement of hydrogen by evaporated films, we have needed a gauge by which the pressure of hydrogen at 10^{-1}–10^{-6} Torr can be measured precisely without any pumping action. For such a purpose, the pirani gauge is one of the most suitable.

GAUGE HEAD DESIGN AND ELECTRICAL CIRCUIT

The gauge head designed and constructed in our laboratory is shown in Fig. 1. Gold coated tungsten wire of 0.01 mm diameter and 10 cm long was used as filament material. The gauge head was painted black

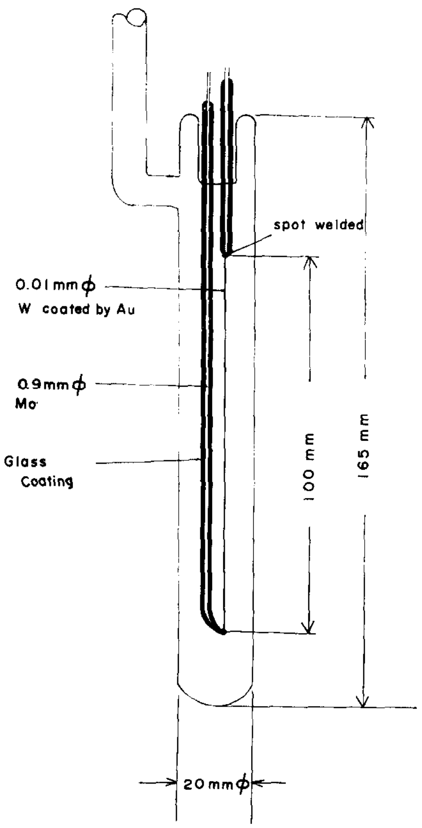

FIG. 1. Head of a sensitive pirani gauge.

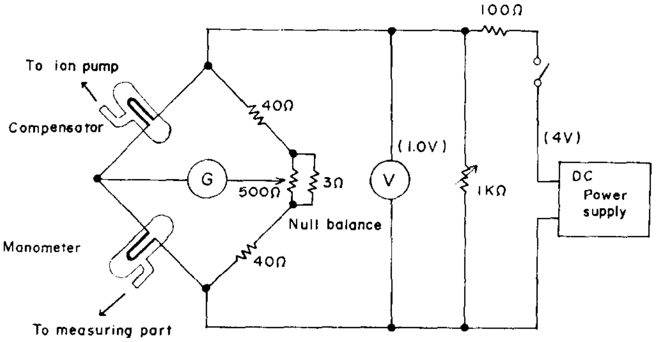

FIG. 2. Electrical circuit diagram for the sensitive pirani gauge.

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for eliminating photoelectric effects. Figure 2 shows the electrical circuit diagram for the sensitive pirani gauge. Direct current potential up to 35 V is generated by the regulated power supply. The input voltage to the bridge is lowered down to a moderate value by a variable resistance. Zero point of the bridge is adjusted with a helical potentiometer. The unbalanced voltage of the bridge is measured with a galvanometer.

ADSORPTION APPARATUS AND PROCEDURE

A block diagram of the adsorption apparatus connected with the pirani gauge is shown in Fig. 3. The method of adsorption measurement at very low pressures is essentially the same as that of the small surface area by xenon adsorption described previously (*1*). The apparatus includes a vacuum system capable of obtaining a pressure of 10^{-9} Torr by a sputter ion pump and two pressure measuring portions A and B in Fig. 3. During the pressure measurement, the metal valve between the gauge head and the sputter ion pump is closed, so that the pressure in the compensating head is always kept in the order of 10^{-9} Torr. Both gauge heads were immersed in a water bath to maintain constant temperature (20 ± 0.5°C).

The pirani gauge was calibrated for hydrogen against a B–A gauge which was calibrated for nitrogen against a McLeod gauge. The sensitivity of the B–A gauge for nitrogen was determined to be 11.2/Torr, and the sensitivity for hydrogen was calculated to be 5.4/Torr using the well known value as specific sensitivity (*2*). During calibration of the pirani gauge for hydrogen, it was necessary to admit hydrogen gas through the variable leak valve to keep a constant pressure, because of large pumping action by the B–A gauge head itself. Calibration was performed for various active gases in the same manner. Figure 4 shows calibration curves with the sensitive pirani gauge for hydrogen in the pressure of 5×10^{-7}–1×10^{-2} Torr. In the figure, logarithm of unbalanced voltage was plotted as a function of logarithm of measuring pressure, and showed excellent linearity. The pirani gauge showed no pumping action for active gases. The time constant for response was about 10 sec at 10^{-6} Torr and 1 sec at 10^{-4} Torr for hydrogen. In addition, the gauge had quite good stability for active gases, particularly the measured points taken at different days were all on one straight line as shown in Fig. 4. The measurements on different gases such as carbon monoxide, carbon dioxide and xenon gave similar calibration curves as that for hydrogen.

ADSORPTION OF HYDROGEN AT VERY LOW PRESSURES

As an example of measurements by the above apparatus, the results of adsorption experiments of hydrogen by evaporated nickel film are presented in the following. Nickel films of about 6000 Å in thickness were prepared by vacuum evaporation. The surface area of the film was determined to

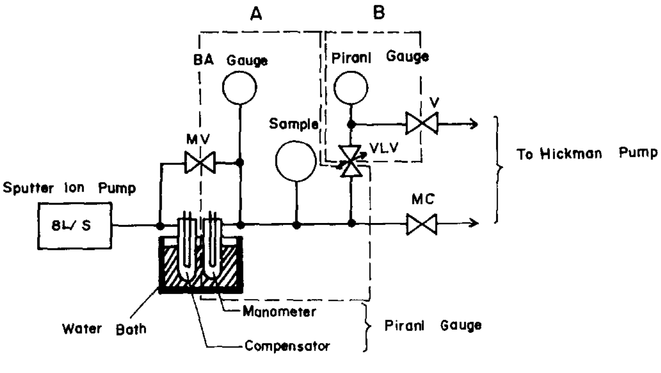

FIG. 3. Block diagram of adsorption apparatus.

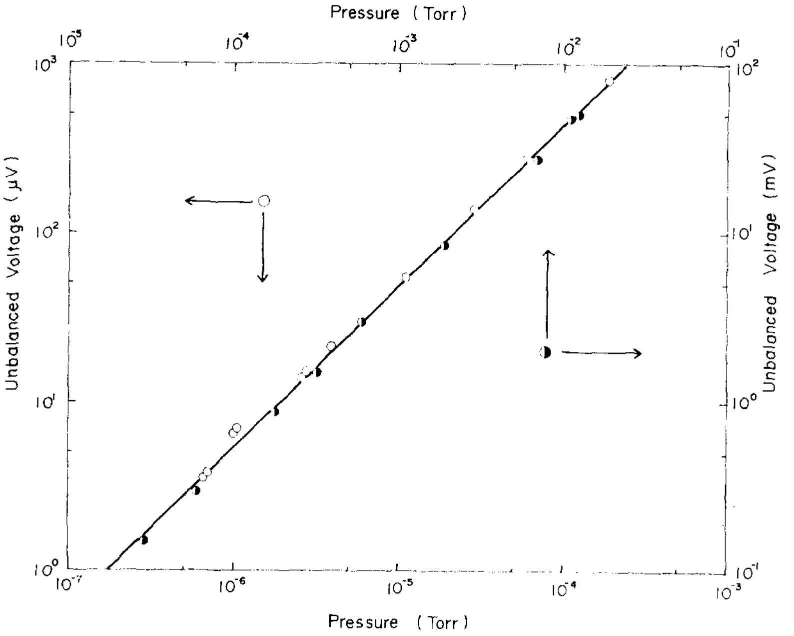

FIG. 4. Calibration curve for hydrogen.

be 415 cm^2 with xenon adsorption by using the same apparatus (the roughness factor was estimated to be 3.38).

The detailed procedure for adsorption measurements is given as follows. After the evaporated film was outgassed until the residual pressure was below 10^{-7} Torr at 450°C, hydrogen gas was admitted into A portion (381 cc) from B portion (566 cc) in which it had been stored in a pressure range of 10^{-3} Torr. After a constant pressure in the A portion had been achieved in one adsorption experiment, hydrogen at higher pressures was added repeatedly.

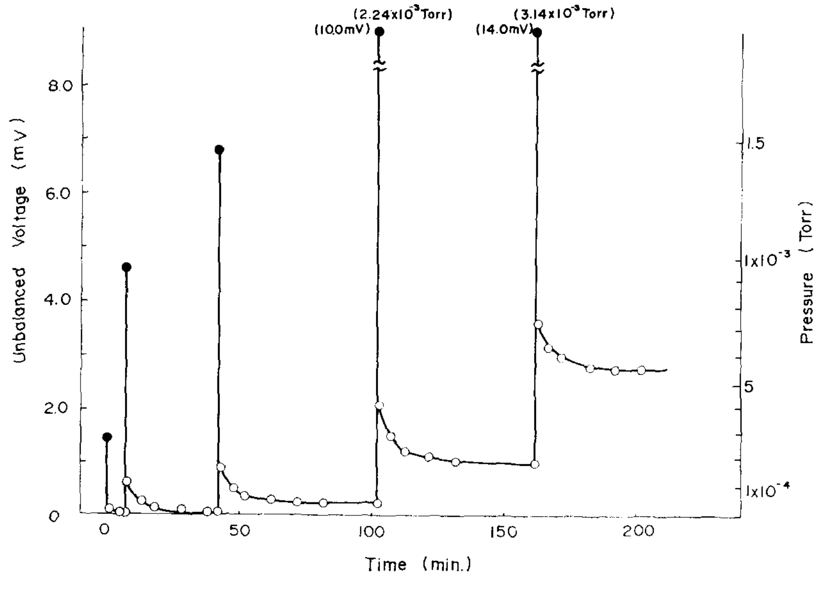

FIG. 5. Example of adsorption process of hydrogen by evaporated nickel film at 23.0°C.

Figure 5 represents the change of pressure with adsorption by the film.

It can be emphasized that the pirani gauge with high sensitivity, no pumping action and excellent stability could be quite useful for the studies of adsorption of active gases at very low pressures. Detailed results of adsorption of hydrogen and different gases by evaporated metal films will be described in the near future.

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Catalytic Properties of Some Mo_3-Cluster Compounds Prepared in High Surface Area

A new class of ternary tetravalent molybdates was reported by McCarroll, Katz, and Ward in 1957 (*1*). The formula for these materials is $M_2Mo_3O_8$, where M = Mg, Zn, Mn, Cd, Fe, Co, or Ni. A striking structural feature is the presence of clusters of three Mo cations bonded together with Mo–Mo separation of 2.53 Å. This close approach (smaller than the Mo–Mo distance in molybdenum metal) indicates strong bonding within the Mo_3 cluster, explaining its weak paramagnetism.

It seemed interesting to investigate the catalytic properties of these materials. However, conventional preparative techniques, (i.e., heating mixtures of reactant oxide powders), gave surface areas of about 1 m^2/g. This was deemed undesirable for catalytic testing. Initial attempts to remedy this involved the use of MgO–MoO_2 powder mixtures with one component present in 2–4-fold molar excess. After formation of $Mg_2Mo_3O_8$, excess oxide was removed with dilute HNO_3. Using firing temperatures of 1100°C, no improvement in product surface area was realized. However, for preparations carried out at 900°C, with either MgO or MoO_2 in excess, $Mg_2Mo_3O_8$ surface areas of 4 m^2/g were achieved. Lowering the firing temperature further did not improve upon this.

A different approach was adopted which gave much better results. It was reasoned that the low surface area obtained for complex oxides by ceramic techniques stems from the relatively large particle size of the starting oxides, typically about 2 μ or more. Reduction of the particle size of either or both oxides would be expected to lead to a lower synthesis temperature and a more finely divided product. A convenient way of effecting this is to start with one of the reactant oxides in high-area (small pore-size) form, and to impregnate this with a solution of a precursor salt of the second oxide. The latter oxide, when formed, will necessarily have particle dimensions no larger than the pore diameter of the first oxide. *Impregnation–synthesis,* as this technique might be termed, thus relies on the fact that high-area oxides, (greater than about 10 m^2/g), will have

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