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Infrared Radiometry of Thermal Transients on Surfaces

An Approach to the Study of Thermal Effects Caused by Gas–Solid Interactions

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A radiometer was used to study the sorption of O_2 on SiO_2-supported Ni. The measurements are based on the premise that the energy produced by the gas–solid interaction heats the surface of the solid, the radiation emitted by the heated surface then being detected. Rapid thermal transients were observed. The method and some preliminary results are discussed.

There has been considerable interest in nonisothermal effects caused by heat generated by gas–solid interactions, and many studies (*1–13*) have appeared since the early work of Damköhler (*1*). Most of these were concerned with "macroscopic" temperatures, e.g., determinations of the temperature differences existing between the exterior surfaces and the interior portions of catalyst pellets, and solutions to such problems have generally been obtained by applying conventional diffusion and heat balance theories to macroscopic catalyst–reactant systems. In contrast, Wei (*11*) considered "microscopic" systems, and attempted to treat temperature effects for surface hot spots of molecular dimensions by means of a rigorous treatment involving a Green's function correlation. However, for a typical cracking catalyst regeneration reaction, a maximum temperature rise of 2°C was predicted by Prater's (*6*) method, while Wei's treatment predicted a possible rise of 34°C for a 2 Å hot spot. Such temperature increases are rather small, and do not appear to be of sufficient magnitude to explain the catalyst sintering which is frequently found during coke burn-off. More recently, Luss and Amundson (*13*) used a shell progressive model to predict a rise of 250°C for coke combustion on a typical cracking catalyst; that temperature rise is more realistic, but also seems not entirely adequate to explain the catastrophic catalyst sintering which is occasionally encountered.

In general, it appears that the mass transport and heat transfer effects involved in a gas–solid interaction are extremely complex, and the precise mathematical description of a physical system has, so far, not been successful. Also, the anomalously high heating rates (*14, 15*) of surfaces observed when solids were exposed to high radiant heat flux suggest that some of the physical aspects of energy transfer at the gas–solid interface are not completely known, so that a rigorous mathematical description may not be possible at this time. We have consequently taken an experimental approach to the problem of surface heating by attempting to measure thermal effects using a contactless, radiometric method, and report some initial observations on surface thermal transients produced by the reaction of oxygen with dispersed nickel.

EXPERIMENTAL METHODS

The apparatus used is shown schematically in Fig. 1. A Kodak Ektron PbS type

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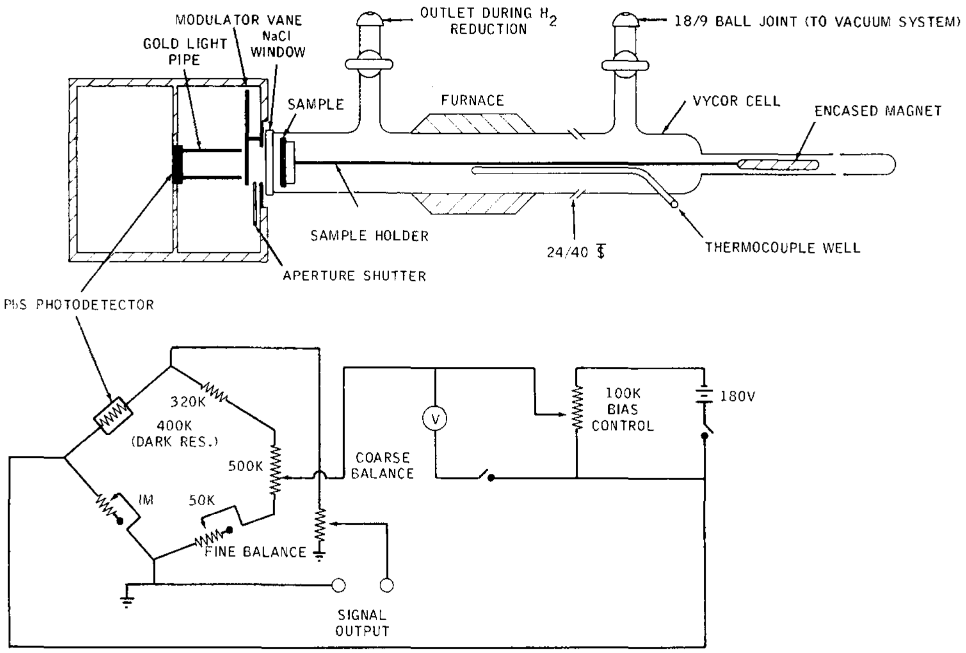

FIG. 1. Schematic of sample cell and radiometer.

N2 detector was used ($D^* = 9 \times 10^{11}$ at $2\,\mu$ at 90-Hz chopping frequency, 100-mm^2 sensitive area). A cylindrical, gold-plated light pipe (9-mm i.d. × 10 mm) was placed between the detector and the cell window. For operation in the unmodulated mode, the signal output (see the lower part of Fig. 1) was directly recorded with a Sanborn oscillograph or, preferentially, displayed on an oscilloscope screen and photographed. The radiometer could also be operated in a modulated mode by using a vane to chop the radiation incident on the detector at 117 Hz. In that case, the signal was enhanced by a General Radio Company Model 1232A tuned amplifier, rectified by a simple diode bridge, and filtered by means of an RC network having a variable time constant. Operation of the radiometer in the more sensitive modulated mode was usually not necessary for the O_2–Ni interaction. The radiometer was calibrated with a standard blackbody emitter similar to that described by Smith *et al.* (*16*).

Adsorbents containing 1, 5, or 10 wt % Ni were prepared (*17*) by impregnating Cab-O-Sil (G. Cabot Co., Boston, Mass.) with aqueous $Ni(NO_3)_2$ solution. Discs of 1-in. diameter weighing approximately 0.3 g were made by pressing the powdered adsorbent at 5 tons/in.^{2} A sample disc, mounted on a movable quartz carriage within the sample cell (Fig. 1), faced the detector. A fresh sample was used for each experiment, except for the one case indicated later. Samples were reduced at 400°C for 12 hr in flowing Pd-diffused H_2, degassed at 10^{-6} Torr at 400°C for 2 hr, and cooled to room temperature *in vacuo*. A known amount of O_2 was then introduced and the radiometric measurement was carried out.

RESULTS AND DISCUSSION

Energy Transfer Considerations

The radiometric measurements are based on the premise that the energy produced by the O_2–Ni interaction heats the surface, radiation emitted by the heated surface then being detected. Emission is considered to predominate at short times and low gas pressures, energy transfer by gas or solid conduction being negligible.

Solid conduction is negligible because of

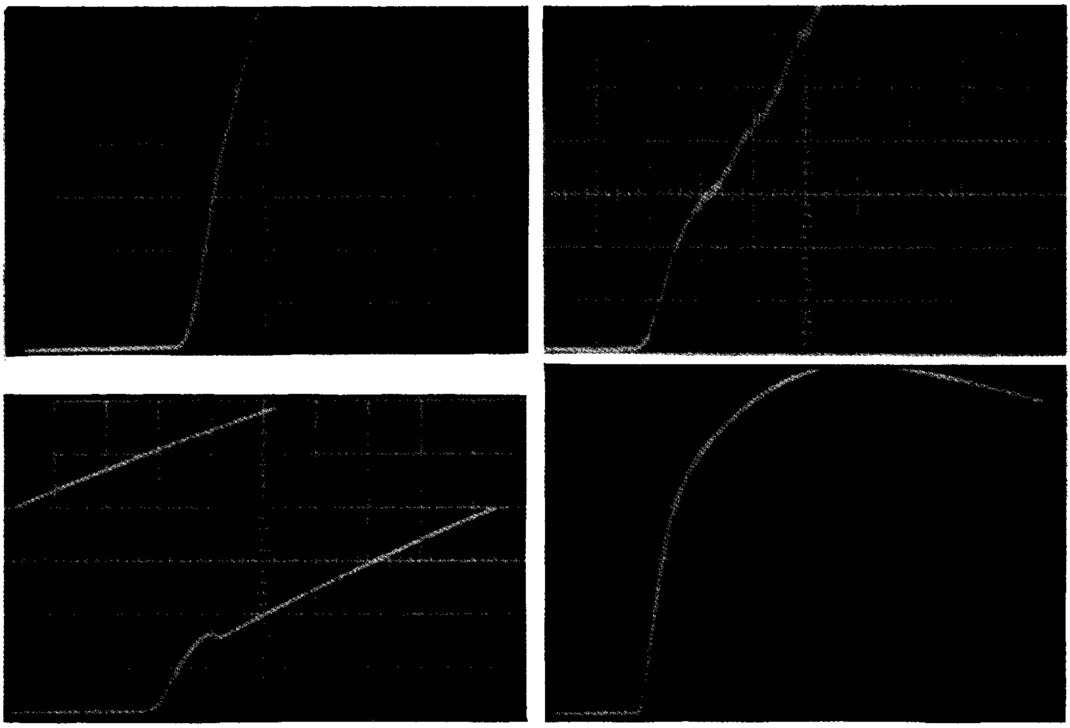

FIG. 2. Typical oscilloscope traces of "radiation curves" resulting from the interaction of O_2 with 10% Ni-Cab-O-Sil: The ordinates are arbitrary and proportional to the temperature of the sample surface. The time base of the oscilloscope was used as abscissa; for A, B, and C, the time base is 500 msec/div; for D, it is 2 sec/div.

the intrinsically low thermal conductivity of Cab-O-Sil, and also because constriction resistance at grain-to-grain contacts imposes a thermal resistance to energy flow because of acoustic mismatch and small-area contacts. Thermal conductivity measurements by Cline and Kropschot (*18*) on metal–Cab-O-Sil mixtures confirm this view. Also, Harrington (*15*) found that the surfaces of solids reached temperatures of 2000°K or more in a few milliseconds, whereas the mathematical theory of heat conduction indicated that several seconds should be required. Observations of a similar nature were made by Kushida (*14*) on irradiating solids with a laser beam. The anomalous heating rates are consistent with results expected for a surface of very low thermal conductivity (*15*). Heat transfer through Cab-O-Sil *via* gaseous conduction was negligible and independent of pressure below 1 Torr; between 1 and 10 Torr it increased only slightly (*18*). In view of these considerations, the assumption that emission was the predominant mode of energy transfer in the present experiments is not unreasonable. Brennan *et al.* (*19*) came to a similar conclusion on studying the calorimetric heats of adsorption of O_2 on Ni films under conditions similar to ours.

If the detected radiation is taken to come from the finely divided Ni and Ni oxide, the hemispherical emissivity values of these emitters must be known, and are assumed to be unity. The difference between the assumed value and values near 0.8 for oxidized Ni sheet (*20*) would lead to an error of several percent in a calculated temperature. However, McAdams (*21*) has indicated that the emissivities of finely divided metals do approach unity, so that errors arising by assuming an improper emissivity value can be expected to be small.

Empirical Relations

Some typical oscilloscope traces are shown in Fig. 2. For smoothly rising curves, such as traces A of Figs. 2 and 3, the maximum temperature rise, ΔT_m (°C), above ambient temperature occurred after 8–12 sec. Such data could be described by:

$$\Delta T = \Delta T_m[1 - \exp(-\omega t^n)], \tag{1}$$

where ΔT is the temperature rise (°C) above ambient temperature at t msec, and ω and n are constants in any one experiment. Equation(1) has the form of a Weibull distribution function (22), so that the constants ω and n may be estimated graphically (23) using Weibull probability charts (Codex Book Co., Norwood, Mass., Chart No. SP-2349), e.g., plot B, Fig. 3, or from plots of log $\log[\Delta T_m/(\Delta T_m - \Delta T)]$ vs. log t. The *rate* of temperature increase computed from plot A of Fig. 3 is given by plot C.

As would be expected, in view of other work on Ni oxidation (24) and O_2 sorption on NiO (25), the thermal effects observed were affected by O_2 pressure. When a 10% Ni adsorbent was exposed to 5.2 or 53 Torr O_2, the ΔT_m values were 144 and 215°C, and the rates (dT/dt at 150 msec) were 480 and 573°C/sec, respectively. The pressure dependence, which was not studied extensively, can be expected to be complex, and can, in part, reflect oxygen diffusion into the NiO lattice during progressive

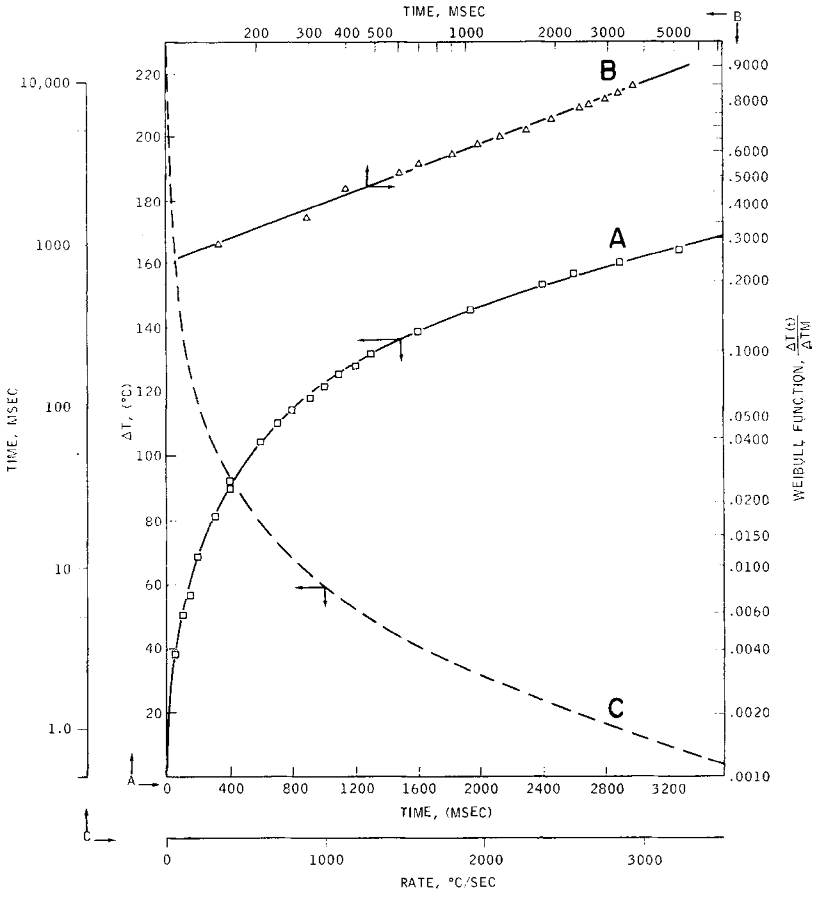

FIG. 3. Oxygen sorption on Ni · SiO_2: (A) $\Delta T - t$ plot, initial O_2 pressure of 1.6 Torr. The data points were taken from an oscillogram; the solid line was calculated using Eq. (1) and the values $\Delta T_m = 200$°C, $\omega = 0.0298$, and $n = 0.05$, derived from a Weibull plot. (B) Weibull plot of the data of line A. (C) Rate of temperature rise calculated using the data of plots A and B and Eq. (1).

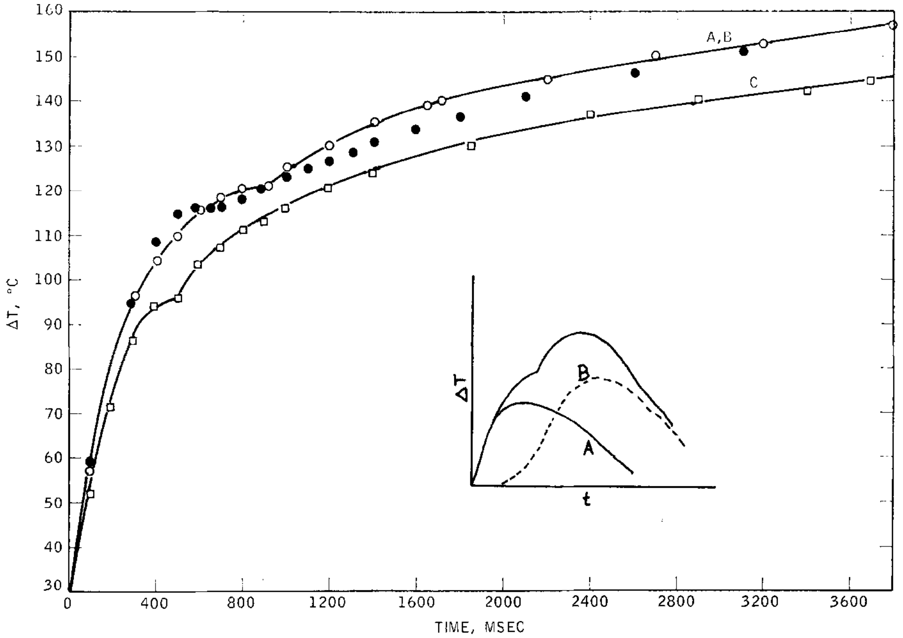

FIG. 4. Repetition of sorption experiment: Fresh adsorbent samples prepared under identical conditions were used for A (○); and B (●); but C was obtained with the same sample used for B. The initial O_2 pressure was 5 Torr. The insert shows, schematically, two overlapping thermal processes.

stages of the bulk oxidation of the metal.

Although Eq. (1) could describe the data over very long time intervals, as in Fig. 3, deviations were frequently encountered. These appeared as small maxima (Fig. 2B) or "stepping" (Fig. 2C) in the oscillograph traces, and would lead to abrupt changes in the slopes of Weibull plots, i.e., changes in the values of the parameters ω and n. In analogy to similar changes found in Elovich plots (*26*), the changes in the Weibull plot and parameters can be ascribed to changes in the mechanism of the sorption processes. The deviations appeared to depend on Ni crystallite size, the degree of reduction, and, in general, on the surface pretreatment. Their precise causes have not been determined but, as mentioned later, a superposition of simultaneous processes may be involved.

Some cooling curves were also measured. The decrease in temperature, ΔT, after ΔT_m had been reached, was well expressed by:

$$\Delta T = \Delta T_m \exp[-k(t - u)^m], \qquad (2)$$

where k, u, and m are constants, and u is the value of t at ΔT_m.

Reproducibility and Sintering

The data were reproducible to within 4% if a fresh sample was used for each experiment, e.g., plots A and B of Fig. 4, but a decline in "activity" occurred when an experiment was repeated with the same sample. After the experiment resulting in plot B had been completed, the sample was subjected to another reducing–degassing cycle, and was then re-exposed to O_2; decreased ΔT_m and dT/dt values resulted (plot C, Fig. 4). The decline in activity can be attributed to a sintering of the finely divided Ni by the highly exothermic chemisorption and oxidation reactions.

Metal Dispersion Effects and Bulk Oxidation

The degree of dispersion of Ni is increased with decreasing Ni concentrations (*17*), so that an increase in activity would be expected if the Ni concentration were decreased. Such an effect was observed. With adsorbents containing 10, 5, and 1 wt % Ni, the respective ΔT_m values were 212, 171, and 137°C, and dT/dt values at $t =$ 100 msec were approximately 200, 300, and 100°C/sec, or 200, 600, and 1000°C/sec/% Ni, although the correction applied to the rates is probably an oversimplification.

Changes in Ni particle size may also be responsible for another variation in $\Delta T - t$ plots. Irregularities or deviations (Fig. 2B; Fig. 4, traces A, B, and C) appeared, much as if there was a superposition of thermal effects. This is shown schematically in the insert of Fig. 4. Process A of Fig. 4 could be the interaction of O_2 with an active, though probably partially oxidized, Ni crystallite surface. Process B could be the bulk oxidation of Ni *via* oxygen incorporation into the Ni oxide lattice (*27*). Such effects would explain the occurrence of "breaks" at lower ΔT and t values when the experiment was repeated with a rereduced (but probably sintered) sample (Fig. 4). If the metal area were reduced, process A would be less extensive and of shorter duration, so that the break would move to lower ΔT and t values.

Such a two-stage model can be considered in terms of what has been called the Penetration Effect (*28*). Ni crystallites ($\langle r \rangle = 100$ Å) react with O_2 to form a nonporous NiO surface phase through which O_2 must continue to penetrate in order to react with Ni. Such a model system can be treated by the Luss–Amundson (*13*) approach to estimate ΔT_m. With appropriate values* for the necessary parameters, the Luss–Amundson equations lead to $\Delta T_m = 320$°C for the present O_2–Ni system, a value not too different from such radiometrically measured ΔT_m values as 240°C.

Kinetics

The radiometrically measured quantities may be used to estimate sorption rates and activation energies. The initial rate of O_2 sorption can be derived from a simple heat balance, if it is assumed that all heat losses from the adsorbent are negligible. This assumption would tend to be valid only in the initial stages of reaction. The rate of adsorption is given by:

$$R = dM/dt = C_p/\Delta H_d \cdot (dT/dt), \qquad (3)$$

where M is the number of oxygen molecules, C_p the specific heat capacity of the Ni, and ΔH_d the differential heat of adsorption. From Eq. (1) and (3),

$$R = k(t) \exp(-\omega t^n), \qquad (4)$$

where $k(t)$ is a slowly varying function of time,

$$k(t) = \Delta T_m n \omega t^{n-1} C_p/\Delta H_d. \qquad (5)$$

For the O_2–Ni system we have found n to lie in the range $0.5 \leq n \leq 1$, so that Eq. (4) has a form similar to the Elovich equation (*28*). For an experiment with a 10% Ni adsorbent at an O_2 pressure of 9 Torr, where $dT/dt = 1000$°C/sec at $t =$ 10 msec, taking $\Delta H_d \simeq 10^5$ cal/mole and $C_p = 0.10$ cal/g/°C, and using a Ni surface area of 13 m²/g catalyst as determined by H_2 chemisorption,

$$R_{10\ \mathrm{msec}} = 4.6 \times 10^{14} \text{ molecules } O_2/\text{cm}^2 \text{ Ni} \cdot \text{sec}. \qquad (6)$$

A collision rate F of 2.4×10^{17} collisions/cm². sec is readily estimated from kinetic theory for O_2 at 9 Torr and 300°K. The sticking probability $S(t) = R/F$ is then 2×10^{-3} at $t = 10$ msec. In view of previous work (*29*, *30*), that $S(t)$ value would indicate that our initial Ni surface was at least partially oxygen-covered; but this is not surprising for a supported Ni catalyst at 10^{-6} Torr. A similar estimate at $t = 900$ msec yields $S(t) = 4 \times 10^{-5}$, indicating a significant decrease in activity; the Ni crystallites were probably well into the bulk oxidation stage where the rate of O_2 uptake had decreased significantly.

The apparent activation energy E can be

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* Values used for calculating ΔT_m using the Luss-Amundson equations were: effective diffusivity, 2×10^{-2} cm²/sec; gas diffusivity, 2×10^{-1} cm²/sec; O_2 conc, 3×10^{-6} mole/cm³; Ni conc, 4.5×10^{-3} mole/cm³; O_2 thermal conductivity, 5.8×10^{-5} cal/cm/°C/sec; Ni thermal conductivity, 1.4×10^{-1} cal/cm/°C/sec; Ni density, 8.90 g/cm³; Ni specific heat, 0.1 cal/g/°C; stoichiometric ratio of solid consumed/mole of gas, 2; heat of reaction, $\simeq 10^5$ cal/g/mole; Schmidt, Prandtl numbers, 2.5.

calculated if simple Arrhenius behavior is assumed. From Eq. (4),

$$[d \ln R/dt]_t = [n(1 - \omega t^n) - 1]/t,$$

and

$$[d \ln R/dt]_t = -[d(1/T)/dt]_t \cdot E/R,$$

so that

$$\begin{aligned} E &= -R[1 - n(1 - \omega t^n)]T^2/t \cdot (dT/dt)_t^{-1} \\ &= \frac{-R[1 - n(1 - \omega t^n)]T^2}{\Delta T_{\mathrm{m}} n \omega t^n} \cdot e^{\omega t^n}; \end{aligned}$$

T is the surface temperature (°C) at time t in milliseconds. For example, using appropriate values,* for $t = 150$ msec and $T = 82°\mathrm{C}$, $E = -120$ cal/mole, and at a later stage at $t = 300$ msec and $T = 106°\mathrm{C}$, $E = -180$ cal/mole. The E values are within experimental error, so that $E \approx 0$, as would be expected for this system.

It will probably be possible to estimate integral heats of adsorption using the radiometric data. A complete radiation curve, i.e., one even more extensive than trace D of Fig. 2, can be described by Eqs. 1 and 2. The energy radiated at any time t, at which the catalyst surface is at temperature T, equals $\epsilon\sigma T^4$ cal/sec·cm², where ϵ is the hemispherical emissivity and σ the Stephan-Boltzman constant, and it can easily be shown that the total energy emitted, Q, due to the sorption process, is:

$$Q = A\epsilon\sigma \int_0^\infty T^4(t)dt \text{ cal},$$

where A is the emitting area. $T(t)$ and the amount of gas adsorbed can be measured, so that the integral heat of adsorption can be approximated. For better estimates it will be necessary to consider the energy required to heat the metal itself as well as the precise geometry of the emitter, e.g., for a metal dispersed over a partially transmitting solid, the "bed depth" or regions below the surface from which radiation could come.

CONCLUSIONS

The present preliminary experiments indicate that surface temperature transients can be detected and recorded by the radiometric technique, and the measured temperature effects can be used to deduce further information concerning the gas–solid interactions. With better detection systems it should easily be possible to record more rapidly occurring transients and to examine less energetic but better defined interactions such as gas adsorption on evaporated metal films. However, in view of the complexity of the thermal and mass transfer effects occurring on and near surfaces, the precise meaning of the actual temperature measurements must be carefully examined in each case in terms of the physical processes and the assumptions involved. For example, greater complexity can be expected for the reaction of a gas with a porous, partly opaque solid, in which case factors such as diffusion into the solid and emission of radiation from below the external surface of the solid will have to be considered. Additional work will be required, but it is hoped that the radiometric data can ultimately be related to the properties of microscopic hot spots or "centers" occurring on catalyst surfaces. Also, such data should be useful for kinetic studies, because rapid temperature changes occurring during the initial stages could affect the kinetics of activated processes, and might alter the nature of the solid in some way so that the initial reaction could exert an influence on later stages of reaction.

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* The values used to estimate E were: ω, 0.03; n, 0.5; ΔT_{m}, 200°C; ambient temp. 25°C.

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