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A COMPARISON OF TGA AND EGD KINETIC DATA USING A HIGH TEMPERATURE OPEN CELL FURNACE

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ABSTRACT

The ability to elucidate solid-state reaction kinetic data employing thermogravimetric analysis (TGA) techniques requires rigid control over the operating parameters, identification of the appropriate rate expression and, when possible, confirmation of the proposed stoichiometry via a second simultaneous method. This task of obtaining kinetic data is further complicated when operating in the 1000°C to 2000°C range and in an open cellular furnace where evolved gas detection (EGD) techniques do not respond directly to sample volatiles because of the gas diffusion throughout the furnace interior. Nevertheless, the most formidable problem to overcome is the occurrence of another weight sensitive reaction concurrent to the desired reaction. This problem of weight sensitive simultaneous reactions necessitated the development of an EGD technique comparable in precision to that of a microbalance for distinguishing a single reaction. The carbothermic reduction of metal oxides model the utility of employing both TGA and EGD thermoanalytical methods and will be shown as viable techniques for derivation of kinetic data.

EXPERIMENTAL

The experiments were conducted with a Netzsch 429 Simultaneous Thermal Analyzer equipped with a 2400°C tungsten resistance furnace and a custom modified gas exit tube[1] allowing for dynamic atmosphere operation at ambient pressure. A Model 202 non-dispersive Infra-Red Analyzer, sensitized and calibrated for carbon monoxide, is coupled to the TGA carrier gas exit.

Mixtures of various metal oxides and graphite were placed in the TGA crucible and heated either in an isothermal or non-isothermal mode. A dynamic atmosphere is obtained by purging with helium.

RESULTS AND DISCUSSION

Reaction rate kinetic data via an EGD technique required a reaction whereby all volatile material was a single component sensitive to detection that would correlate to weight loss. The carbothermic reduction of metal oxides is expected to liberate

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only CO while forming the metal carbide. In the case where Ta_2O_5 is heated with excess carbon

$$Ta_2O_5 + 14C \longrightarrow 2TaC + 7C + 5CO$$

the exit gas from the TGA/IR was analyzed for the presence of CO_2, but none was found. The post-analysis residue contained only TaC and graphite. A good correlation between weight loss and CO detected was anticipated, but in fact CO was detected far beyond the point where the weight stabilized. This tailing effect was attributed to the diffusion of the sample effluent in the open-cell furnace. A means for correcting the CO curve for diffusion in the TGA was attempted by using a deconvolution mathematical correction using the mean residence time such as that used in modeling a back-mixed reactor[2]. To determine the applicability of this technique, several standard CO-He gas mixtures were injected directly into the furnace. Deconvolution of the resulting curve showed three distinct areas of response for CO correlating to three paths of different length for the gas to reach the detector. These paths could very well be caused by the longitudinal opening in the heating element and a hole in the three concentric radiation shields[1], causing complex flow patterns inside the furnace.

By trial and error, a mean residence time of 1.5 minutes was found to be suitable for deconvolution of CO curves, resulting in the detected weight loss and the detected CO (converted to weight) to be within a 0.5% maximum difference over a 20% cumulative weight/CO loss from 1200°C to 1650°C. The mathematical correction for CO deconvolution due to gas diffusion in the furnace is:

$$[CO]^t_{\text{corrected}} = [CO]^t_{\text{observed}} + t_r \frac{d[CO]^t_{\text{observed}}}{dt} \qquad (1)$$

$$Y = \sum_{t=0}^{e} \frac{[CO]^t_{\text{corr}}}{100} \times \text{He} \times \frac{1 + [CO]^t_{\text{corr}}}{100} \times 1.0423 \times 10^{-3} \text{g CO/cc} \qquad (2)$$

where $[CO]^t$ = CO concentration at time t in volume %
t_r = the average residence time of 1.5 minutes
Y = total CO evolved in mg
t = o is the beginning of the experiment
t = e is the end of the experiment
He = helium flow rate in cc/minute

The ability to quantitatively determine the amount of a specific gas (CO) evolved from a sample has been demonstrated, but extending this to elucidate kinetic rate data solely from a gas detector must be proven. To accomplish this, another metal oxide, silica, was reacted with graphite

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

to form silicon carbide and liberate carbon monoxide. As in the former reaction, the weight loss and CO detected (corrected by deconvolution) should coincide. The computed reaction rates should also agree. To simplify the determination of rate data, measurements were taken isothermally at 1560°C, 1610°C and 1660°C. Rate constants were calculated by testing a common expression based on homogeneous first-order kinetics[3]:

$$\ln \frac{W_o}{W_o - X} = k_1 t \qquad (3)$$

where k = rate constant for a given temperature, sec^{-1}

W_o = initial weight of reactants

X = decrease in weight of reactants

t = seconds elapsed during the measured weight loss interval

In Table I, the results of these studies are summarized. The higher the isothermal temperature, the greater the rate of reaction and the greater the amount of material reacted prior to reaching the desired temperature. Even heating at 100°C/min., to

TABLE I. A COMPARISON OF REACTION RATES DERIVED FROM SIMULTANEOUS TGA & IR DETECTION ON THE REACTION $SiO_2 + 3C \longrightarrow SiC + 2CO$

	Extent of Reaction						
	Prior to Isothermal Temperature		Linear Response ln (wt.reactants) vs Time		Reaction Rate $k \times 10^4, sec^{-1}$		Deviation IR from TGA
Isothermal Temperature	TGA	IR	TGA	IR	TGA	IR	TGA
1560°C	2%	12%	5-87%	12-34%	13	12	-6%
1610°C	5	7	5-90	10-60	26	24	-6
1610°C	5	17	5-72	17-65	28	32	+11
1610°C^a	9	10	32-68	13-47	7	8	+6
1660°C	17	22	9-86	15-86	47	39	-17
1660°C^a	29	30	33-80	45-81	37	44	+21

a = lid on crucible

1660°C, up to 30% of the reactants were expended prior to the desired temperature, allowing very little time (<5 minutes) for monitoring the reaction. Nevertheless, even at these fast rates a linear response was found, until 80-86% of the reactants were expended, when tested against the rate expression (Equation 3).

The reaction rate constants based on the simultaneous TGA and EGD techniques even at these very fast rates deviated in the 17% to 21% range. The agreement was much better at the lower temperatures of 1560°C and 1610°C, where the mean deviation between the two techniques for four runs was less than 8%.

Finally, an Arrhenius plot for the TGA and EGD four data points (open crucible) listed in Table I yielded activation energies of 84 and 90 kcal/mole for the weight and CO respectively ... a 7% deviation.

CONCLUSION

Reliable kinetic parameters, reaction rate constants, activation energies may be obtained from sample effluent when evolved into an open-cell furnace operating in the 1000°C to 2000°C range. Back-mix reaction calculations reliably deconvolute the delayed He-CO mix from the sample crucible to the gas detector. The utility of this EGD procedure will be invaluable when a concurrent weight sensitive reaction prevents discrimination of the data by TGA.

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