MASTER

CONDENSATION PROCESSES
IN COAL-COMBUSTION PRODUCTS

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ABSTRACT

Slag vaporization is a serious problem in high-temperature coal combustion and gasification processes. Cooling of process gas streams causes the slag vapors to condense, but they do not necessarily do so at equilibrium. Predicting the compositions and properties of the condensing species requires modeling these nucleation processes occurring in these systems.

This is a report of our progress toward modeling the nucleation processes, implementing the model with a computer code suitable for design calculations, and testing the model with appropriate experiments.

This research program concerns the rate of condensation nucleation when a phase transition accompanies a chemical reaction. Our efforts are aimed at modelling such a process, developing a computer code to facilitate the use of this model by process and design engineers, and verification of this model with appropriate experiments. It is believed that our experiments will yield data that is also useful to others concerned with related energy technology problems.

We have developed a theory which describes the rate of nucleation when a phase transition accompanies a chemical reaction. This theory is applicable to the crystallization of ionic species from solution, to the formation of a non-volatile product as a result of the reaction of two or more gaseous species, and to the formation of an immiscible liquid by reaction of soluble species. The theory is capable of treating chemical reactions that occur both homogeneously in the bulk parent phase, and heterogeneously on the surfaces of previously formed clusters.

The nucleation rate expression depends on a number of system conditions including: the rate of condensation relative to the rate of reaction, the rate of homogeneous reaction relative to the rate of heterogeneous reaction, the equilibrium extent of conversion, and the solubilities of the gaseous reactants in the condensed product. We have determined the rate of nucleation for a number of combinations of these variables; these are discussed in the attached reprint.¹

We have applied this theory to predict the rate of condensation nucleation for silica (SiO_2) at high temperatures. Our calculations were made using our modified version of Gordon and McBride's NASA computer program². We have shown that there are dramatic differences among the rates of nucleation predicted for three different cases: assuming no chemical reaction, assuming homogeneous nucleation of an equilibrium mixture of SiO and SiO_2 , and assuming the chemical reaction occurs both homogeneously in the gas phase and heterogeneously on the surfaces of previously formed nuclei. We have also shown that for the SiO_2 system, the type of nucleation (homogeneous or chemical) depends strongly on the combustion temperature and on the amount of oxygen (relative to stoichiometric) present in the system.

Our results are shown in Figures 1 to 3. The results are for the adiabatic combustion of silane in argon by oxygen. Hydrogen is used to control the flame temperature, and the conversion of SiO to SiO_2 is controlled by the ratio of O_2 to H_2 relative to stoichiometric.

Figure 1 shows the adiabatic flame temperature as a function of the mole ratio of oxygen to hydrogen for various concentrations of argon. In these calculations, the contribution of the heat of combustion of the silane was included, but is negligible. As expected, one sees that the maximum flame temperature occurs at the stoichiometric ratio of O_2 to H_2 , and that this maximum temperature decreases as argon is added. Figure 2 shows the mole ratio of SiO to SiO_2 in the vapor phase as a function of temperature

for various mole ratios of oxygen to hydrogen. For SiO to SiO₂ mole ratios which are much greater than 1, the rate of nucleation should be controlled by the rate of chemical reaction. For mole ratios less than 1, the nucleation should be essentially the homogeneous nucleation of pure SiO₂, independent of the rate of chemical reaction.

The rate of nucleation depends on the thermodynamic driving force (the amount of undercooling), the rates of gas-phase and surface chemical reaction, and the extent to which the reactant molecules adsorb on the surfaces of nuclei of the condensing product. For the condensation of silica, under the conditions present in most flue gases, we expect the rate of gas-phase reaction to be very fast. We therefore assume that the vapor-phase concentration of SiO₂ is determined by its chemical equilibria with SiO and oxygen. The rate of nucleation still depends strongly on the rate of surface reaction as shown in Figure 3. In Figure 3, the nucleation temperature is given as a function of total moles of all silicon containing species (i.e., Si, SiO, SiO₂, Si(OH)₄) for various values of the reaction rate constant. These calculations are for a stoichiometric amount of SiO and O₂ at a SiO concentration typical of a high temperature coal combustion process (mole fraction of 0.0001). Our calculations show that as the surface reaction rate constant increases, nucleation occurs at a higher temperature (i.e., lower supersaturation) for a given silicon concentration. Figure 3 also shows the effect of the adsorption isotherms. We assume that SiO₂

molecules cannot condense or evaporate from that portion of the nucleus surface covered by adsorbed SiO or oxygen molecules. Again, one sees an increase in the nucleation temperature. To make these calculations, a number of assumptions and estimations are necessary. We feel these are reasonable and justified, but probably will be improved upon in the future as more data become available.

The thermodynamic properties of silane in the ideal gas state reported in the JANAF Thermochemical Tables (1978 Supplement) were fitted to a polynomial to allow inclusion in our computer program. For the temperature range of 1000 K to 3000 K the properties are:

$$\frac{C_p^0}{R} = 2.1787 + 1/3741(10^{-2})T - 7.4922(10^{-6})T^2 + 1.9352(10^{-9})T^3 - 1.9335(10^{-13})T^4$$

$$\frac{H^0}{RT} = 2.1787 + 1/3741(10^{-2})T - \frac{7.4922(10^{-6})}{3}T^2 + \frac{1.9352(10^{-9})}{4}T^3 - \frac{1.9335(10^{-13})}{5}T^4 + \frac{2.7930(10^3)}{T}$$

$$\frac{S^0}{R} = 2.1787\ln(T) + 1.3741(10^{-2})T - \frac{7.4922(10^{-6})}{2}T^2 + \frac{1.9352(10^{-9})}{3}T^3 - \frac{1.9335(10^{-13})}{4}T^4 + 8.1071$$

The surface tension of liquid silica had to be estimated.

Although there is considerable experimental data for silica and

silica mixtures at lower temperatures, no experimental data are available for the conditions we are studying. The surface tension was estimated to be

$$\sigma = 0.2524 + 3.5(10^{-5})(T - 273.15)$$

The greatest uncertainty in our calculations is due to lack of knowledge concerning the rate of heterogeneous chemical reaction. This can be treated as a parameter with which one can fit the experimental data we plan to generate, but it may be preferable if this could be determined independently so that a critical test of the theory could be made.

We have also made calculations and run experiments on the nucleation of borane-dimethylsulfide. This compound exists as the solvated complex in the liquid phase but dissociates to dimethyl sulfide and borane (which likely associates to diborane) in the vapor. Experiments were performed using an upward thermal diffusion cloud chamber. The diffusion cloud chamber is designed so that, to a high degree of approximation, one-dimensional diffusion takes place through a carrier gas from a hotter to a cooler layer of vapor. It consists of a warm bottom plate and a cooler top plate separated by a glass ring which is sealed by rubber gaskets to both plates (see fig. 4). The bottom plate is covered by a liquid pool of the substance under investigation. Vapor evaporates from the top surface of the pool, diffuses upward (through a light carrier gas so that the total gram density ρ_t of the vapor and carrier-gas mixture decreases from the bottom of the

chamber to the top (see fig. 5) thus preventing convection), and condenses on the bottom surface of the top plate.

The temperature T and the partial pressure P decrease approximately linearly with increasing height. An iterative computer solution of the equations for the heat and mass flux provides accurate temperature and partial-pressure profiles. The equilibrium vapor pressure P_e is approximately an exponential function of temperature and decreases more rapidly with increasing height than does the actual partial pressure of the vapor. At any plane in the chamber, characterized by temperature T , the actual partial pressure P of the vapor is greater than the equilibrium vapor pressure P_e at that temperature. Thus the supersaturation P/P_e is unity at the top and bottom surfaces and is greater than unity in between, reaching its maximum value near the top of the chamber (see fig. 5). By increasing the temperature gradient this supersaturation maximum can be made as large as desired.

The onset of homogeneous nucleation is determined visually by observing the forward scattering of light by drops. The drops appear at a fairly well-defined plane, usually about 85% up from the bottom to the top plate, and fall to the bottom. When the temperature gradient is not large enough, only the occasional clusters of drops due to ions can be observed. The desired gradient is that one which is just large enough to produce homogeneous nucleation, i.e., at a well-defined horizontal plane in the chamber (slightly lower than the plane for maximum supersaturation) the vapor is just sufficiently supersaturated so that

the desired number of randomly scattered falling drops (usually $2-3 \text{ cm}^{-3}$) appear.

The chamber is self-cleaning. Once a dust particle has nucleated a drop, the drop rapidly grows to visible size, falls down to the liquid pool, and the dust particle is then trapped in the liquid by surface forces. The chamber effectively has "no" top and bottom walls in the sense that it is supersaturated only in its interior. The side wall (i.e., the glass ring) is "infinitely" far away from the region of observation; "infinitely" far is a diameter-to-height ratio of 5 or greater. Experiments were repeated with the walls farther and farther away (actually the top and bottom surfaces were moved closer and closer together) and produced identical results.

Our laboratories have several cloud chambers which are also being used to study homogeneous nucleation and the effect of light on the rate of homogeneous nucleation. Experiments to date on borane dimethylsulfide are preliminary and show more scatter than expected. Our theoretical predictions do not agree with what data we have, but this could be due to uncertainties in the surface tension of borane dimethylsulfide, uncertainties in the rate of diffusive mass transfer due to the chemical reaction, or experimental error. One question about our experimental results that is yet to be answered concerns the possible absorption of dimethylsulfide in the gasket material used in the cloud chamber.

REFERENCES

1. J.L. Katz and M.D. Donohue, "Nucleation with Simultaneous Chemical Reaction", submitted to Journal of Colloid and Interface Science.
2. S. Gordon and B.J. McBride, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations", NASA #N71-37775, Washington, D.C. (1971).

FIGURE 1

Adiabatic flame temperatures as a function of oxygen to hydrogen mole ratio for various dilutions with argon.

FIGURE 2

Mole ratio of silicon monoxide to silicon dioxide as a function of temperature for various mole ratios of oxygen to hydrogen in the fuel. For mole ratios of SiO to SiO₂ greater than one, chemical nucleation occurs, while for mole ratios of SiO to SiO₂ much less than one, pure-component homogeneous nucleation occurs.

FIGURE 3

Nucleation temperature as a function of the sum of the partial pressures of all silicon containing species for various surface coverages and various surface-reaction rate constants.

(1) $\theta_c = 1.0$, therefore independent of surface-reaction rate constant.

(2) $\theta_c = 0.8$, $ks_{asb} = 10^{18}$ molecules $\text{sec}^{-1} \text{atm}^{-2}$.

(3) $\theta_c = 0.7$, $ks_{asb} = 10^{18}$ molecules $\text{sec}^{-1} \text{atm}^{-2}$.

(4) $\theta_c = 0.8$, $ks_{asb} = 10^{19}$ molecules $\text{sec}^{-1} \text{atm}^{-2}$.

(5) $\theta_c = 0.7$, $ks_{asb} = 10^{19}$ molecules $\text{sec}^{-1} \text{atm}^{-2}$.

FIGURE 4

Upper: a schematic representation of homogeneous nucleation caused by the vapor evaporating from the liquid pool, diffusing through the carrier gas, and condensing on the upper conical surface. Lower: an example of the variation with reduced chamber height of ρ_a , the density of the vapor; ρ_b , the density of the carrier gas; ρ_t , the total density ($\rho_t \equiv \rho_a + \rho_b$); T , the temperature; P , the partial pressure of the vapor; $P_{carrier\ gas}$, the partial pressure of the carrier gas; P_e , the equilibrium vapor pressure at the gas temperature T ; and P/P_e , the supersaturation. Illustrated with data on nonane-helium.

FIGURE 5

Cutaway view of the diffusion cloud chamber.