

Figure 8. Monolayer surface adsorption correlation

more difficulty than molecules of lesser dimensions. Further, the lower the temperature, the less energetic is a gas molecule, *i.e.*, the lower its average translational motion.

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Phase Relationships for the AgNO₃-AgI-AgIO₃ System

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 \mathbf{I}_{N} THE REPROCESSING of spent fuel elements from reactors, gaseous products are liberated which include radioactive iodine. To remove this iodine, a tower consisting of silver nitrate coated on ceramic packing is used (6). The reactions conditions are in the range of 200° C. and 1 atm.

The over-all equation in unbalanced form is:

$$AgNO_3 + I_2 \rightarrow AgIO_3 + AgI + NO_2$$
(1)

The reaction mechanism is uncertain. Blasewitz and Schmidt (1) report a series of reactions as follows:

$$2AgNO_3 + I_2 \rightleftharpoons 2AgI + O_2 + 2NO_2$$
⁽²⁾

$$AgNO_3 + \frac{1}{2} I_2 + O_2 \rightleftharpoons AgIO_3 + NO_2$$
(3)

$$AgIO_3 \xrightarrow{\Delta} AgI + \frac{3}{2} O_2$$
(4)

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They further state that AgI is the thermodynamic stable end-product when the reaction is run at 200° C.

Lacksonen (5) has shown conclusively that $AgIO_3$ is stable in the presence of dry air or helium in the pressure range of 1 to 760 mm. of Hg and for temperatures as high as 330°C. No decomposition was noted in the presence of AgI or AgNO₃. Dupuis and Duval (3) report a decomposition temperature of 410° C. without melting. Silver iodide has a decomposition temperature of 552°C. without melting, and AgNO3 melts at 211° C. without decomposition (4).

In studying the kinetics of the I_2 (v) – AgNO₃ (s or 1) reaction, Lacksonen (5) experimentally measured the mole ratio of $AgIO_3/AgI$ and compared the results with a theoretical maximum ratio of 0.5 if all of the oxygen liberated via Equation 2 reacts as in Equation 3 with Equation 4 not kinetically applicable. These experiments showed that the AgIO₃/AgI ratio was always lower than the maximum value of 0.5. It dropped to as low as 0.22 and was dependent on the physical state of the reacting zone. Hence, the temperature-composition phase diagram for the AgI-AgIO₃-AgNO₃ ternary was necessary in the interpretation of the kinetics of the reaction.



Diagram for AgIO₃-AgNO₃

EXPERIMENTAL

Reagent grade chemicals were used. Freezing points were obtained by the usual cooling curve slope-inflection method. The solids mixture of about 4 gms. was placed in a 10×75 mm. test tube which was inserted in a 1-liter stainless steel beaker. The heat transfer media was mineral oil up to 215° C. and molten salt (53% KNO₃, 40% NaNO₂ and 7% NaNO₃) above 215° C. The ambient condition was air at 1 atmosphere pressure. A 24-gage iron-constantan thermocouple immersed in the ternary mixture plus a continuous strip-chart recorder was the temperature monitoring system to obtain slope changes at the freezing point.

RESULTS

The temperature-composition data for the binary $AgIO_3$ - $AgNO_3$ are plotted in Figure 1. Above 65 weight % $AgIO_3$, a true solution could not be obtained at 300° C. the highest temperature used. A number of ternary compositions were analyzed in this manner. The lowest melting eutectic occurred at a weight per cent composition of 50% AgI-27% $AgNO_3-23\%$ $AgIO_3$ with a melting point of 76° C. This information, coupled with the data of Bokhovkin (2)



on the AgNO₃-AgI binary was sufficient to prepare a ternary diagram as Figure 2 with isotherms sketched in to show phase relationships from the eutectic point at 76° C. up to 300° C. Since all three salts contain monovalent anion and cation constituents, the relatively simple phase diagram as observed would be predicted.

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