A General Theory for the Kinetics of Intercalation of Graphite

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Abstract. A general theory, which takes into account the evaporation, transport and condensation of the intercalate outside the graphite and the diffusion and staging inside the graphite, is presented for the kinetics of intercalation of graphite. The theory has been applied to a number of intercalates (including Br, ICl, K, Rb, Cs, $FeCl_3$, $NiCl_2$, $CuCl_2$, $PdCl_2$, HNO_3, AsF_5 and SbF_5) at various temperatures.

1 Introduction

Intercalation reactions may be better understood if the process of intercalation is subdivided into individual reaction steps. If this is done, the individual steps can be analyzed to determine their influence on the reaction kinetics.

2 Reaction Steps

The intercalation process can be broken up into several steps, any of which can be rate controlling depending on the reaction conditions. In general, a reaction may be controlled by a reaction at an interface or by the transport between interfaces. In the particular case of intercalation the overall reaction may be broken up into several steps:

1. evolution of a transportable species, in the case where the reservoir of the intercalate is a separate phase from the transport medium;
2. transport of the intercalate to the surface of the sample;
3. adsorption of the intercalate onto the surface of the sample from the transport medium;
4. insertion of the intercalate into the sample;
5. diffusion of the intercalate through the sample;
6. the staging reaction occurring at the interface between the initial stage and the pristine graphite, or between one stage and the previous stage.

We have calculated the time needed for these steps for the following intercalates: bromine, iodine monochloride, nitric acid, potassium, rubidium, cesium, iron(III) chloride, nickel(II) chloride, copper(II) chloride, palladium(II) chloride, arsenic pentafluoride and antimony pentafluoride. The assumption was made that the two-bulb method was used for intercalation, with 30 cm separation between the intercalate reservoir and the graphite sample, and with the whole system at the same temperature. The sample was assumed to have the dimensions of 4 mm x 12 mm x 0.5 mm. Bromine, iodine monochloride and nitric acid were assumed to be intercalated in one atmosphere of nitrogen; the alkali metals and pentafluorides were assumed to be intercalated in vacuum; the metal halides were assumed to be intercalated in chlorine at the equilibrium dissociation pressure.

The time necessary for a given reaction step can be calculated from knowledge of the physical properties of the intercalates. The heat of vaporization (or sublimation) is the principle factor in determining the evaporation and condensation rates, while the presence of an ambient gas most affected the rate of transport of the intercalate from the intercalate reservoir to the sample. It was assumed that if surface reactions existed, the time needed for the surface reaction was negligible. Estimates for the in-plane diffusion coefficients were based on an empirical correlation of the diffusion coefficient with the melting point [1, 2]. If the intercalate species was ordered at the reaction temperature the diffusion coefficient was estimated as the self-diffusion coefficient in a solid; if the intercalate was not ordered, the diffusion coefficient was estimated as the self-diffusion coefficient in a liquid. The staging reaction was assumed to have an Arrhenius temperature dependence, using the same activation energy as the diffusion coefficient and a pre-multiplier determined from the staging reaction rate in bromine-graphite compounds.

3 Relative Significance of the Reaction Steps

Figure 1 compares the relative significance of the different reaction steps in the overall reaction time. Since a wide range of temperatures was considered, the times for an individual step vary over several orders of magnitude between the different intercalate species. To compare the relative importance of the individual reaction steps for the different intercalates, the reaction time for an intercalate was totaled and the amount of time relative to the total time was plotted.

Bromine and iodine monochloride intercalate as ordered structures and consequently exhibit slow diffusion through the sample, with the result that diffusion control is expected.

The calculations for the alkali metals indicate that no single reaction step is clearly rate controlling. The indication of a mixture of controlling steps is supported by reports on the kinetics of alkali metal intercalation. Aronson and Salzano [3] indicated that the desorption of cesium from graphite intercalation compounds is controlled by the evaporation rate of cesium from the surface of the graphite. Pfluger et al. [4] indicated that the intercalation of alkali metals cannot be described adequately by a single reaction mechanism. Hamwi et al. [5] suggested that the kinetics of intercalation of potassium could be described by an empirical law of the form L = a exp(bt), where t is is the time, a is a normalization constant, L is the penetration length of the intercalate and b is the slope of the line defined by plotting ln L versus time.

The calculations for the metal halides indicate that the evaporation and condensation of the intercalate on the sample is most likely to be the limiting reaction steps, which is in keeping with the low vapor pressure at the reaction temperature. It may be possible to set up the reaction so that the metal halide is complexed with excess halogen to form a more volatile halide. If the halide complex decomposes at the sample surface,
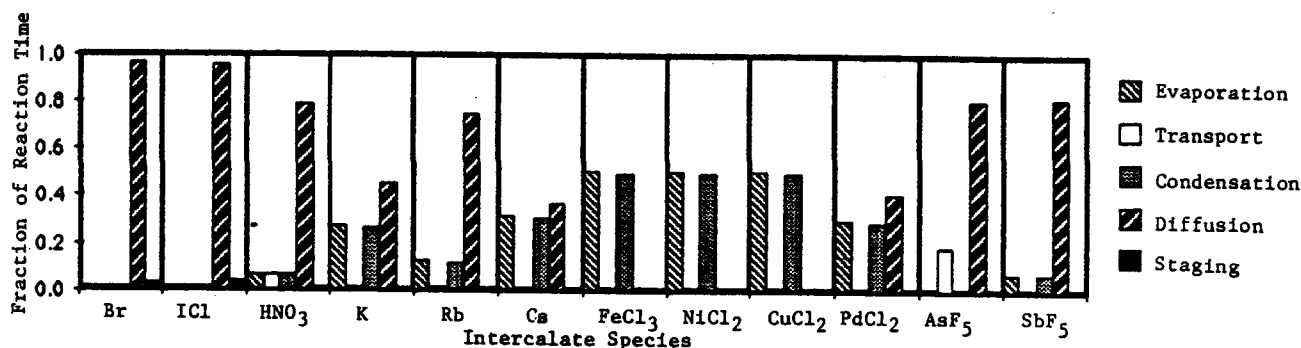
Figure 1.   The fraction of time needed for each reaction step for various intercalate species.
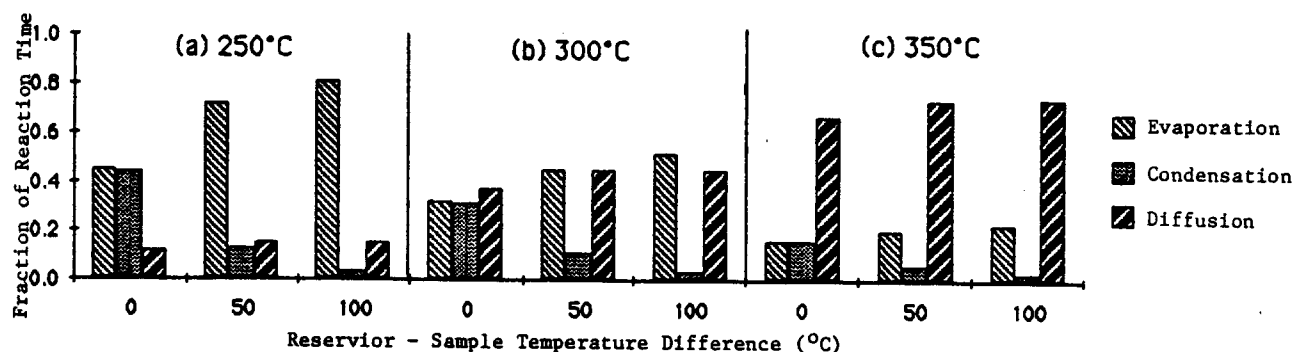

Figure 2.   The fraction of time needed for the dominant reaction steps in the intercalation of cesium in graphite with 0, 50 and 100°C temperature differences between the cesium reservoir and the graphite sample. (a) Cesium reservoir at 250°C (b) Cesium reservoir at 300°C (c) Cesium reservoir at 350°C.

the net transport rate of the metal halide can be increased [6, 7, 8]. Such a complexing reaction is not taken into account in this approximation of the transport step. Nonetheless, Flandrois [9] investigated the intercalation of nickel chloride and concluded from the kinetics and the activation energy that the reaction controlling step was either evaporation or condensation. The same conclusion was reached by Dowell and Badorrek [10] in a study of the intercalation of palladium chloride in graphite.

Nitric acid, arsenic pentafluoride and antimony pentafluoride form a special group. For these compounds the active intercalating agent is formed by the dissociation of the initial intercalate. Figure 1 indicates that all three should be diffusion controlled. However, the analysis ignores the possibility of a surface reaction other than adsorption, and is therefore probably not appropriate for these compounds with marked dissociation. Experimentally it seems that for these compounds a surface reaction may be the limiting step. Forsman indicated that a surface reaction may be the controlling step in the intercalation of nitric acid [11]; Hooley [12] observed that the intercalation rate of arsenic pentafluoride is markedly different between the first intercalation rate and that obtained by desorbing the sample and subsequently re-intercalating.

The effect of varying the temperature of the system, or having the intercalate reservoir and sample at different temperatures is indicated in Figure 2. This figure illustrates the change in the relative importance of reaction rates for the intercalation of cesium. Reaction times were calculated for intercalate reservoir temperatures of 250, 300, and 350°C, with reservoir-sample temperature differences of 0, 50 and 100°C for each reservoir temperature. The primary effect of increasing the reservoir temperature is to make the diffusion step dominate the reaction. This is due to the fact that the activation energy for diffusion is smaller than the heat of vaporization. As the temperature increased, the vapor pressure

of cesium increases more rapidly than does the diffusion rate, so that the time for evaporation becomes short compared to the time needed for diffusion into the sample.

The principle factors in determining the intercalation rate appear to be the diffusion rate of the intercalate within the sample and the vapor pressure of the intercalate. Low vapor pressures of the intercalate imply slow evolution times of the intercalate from the reservoir. Surface reactions may also be rate-limiting, but are very difficult to estimate a priori.

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