MEMORANDUM ON CHEMICAL REACTIONS
AND REACTOR HAZARDS
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MEMORANDUM ON CHEMICAL REACTIONS AND REACTOR HAZARDS

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INTRODUCTION

Two important problems in the investigation of reactor hazards are the chemical reactivity of various materials employed in reactor construction and the characteristics of heat transfer under transient conditions, specifically heat transfer when driven by an exponentially increasing heat source (exp t/T).

Although these problems are independent of each other, when studied in relation to reactor hazards they may occur in a closely coupled sequence. For example, the onset of a dangerous chemical reaction may be due to structural failure of various reactor components under an exponentially rising heat source originating with a runaway nuclear reaction. For this reason, these two problems should eventually be studied together after an exploratory experimental survey has been made in which they are considered separately.

CHEMICAL REACTIVITY

The methods of chemical thermodynamics may be employed to determine whether or not any given chemical reaction will proceed. Some pertinent reactants may be listed from the first issue of Reactor Science and Technology (last section on the status of reactor development). This list, with some additions, is as follows:
This list is not meant to be exhaustive, but indicative. Even so it is clear that the number of possible reactive pairs, triples, etc. is very large. Some selection of materials for experimental study must be made. The chemical systems U + 2H2O, Zr + 2H2O seem to be a good place to start.

In the Appendix there is given a survey of the theoretical decrease in free energy for various pairs of reactants for a range of initial reaction temperatures. This merely begins the study since thermodynamic results indicate little about reaction rates. In the case of reactor hazards, the possible occurrence of explosive reaction rates is of primary concern. In NAA-SR-31 it was pointed out, that if the possible chemical reactions go to completion, that chemical energy sources may greatly exceed the energy release of the runaway nuclear reaction.

An experimental study of reaction rates, for chemical systems which can react according to free energy considerations, is needed. The problem is more complex than simple chemical kinetics in the gas phase. Most of the chemical systems pertinent to reactor problems consist of heterogeneous mixtures of reactants in the liquid or liquid and solid phase. The reacting atoms must come together by a process of mixing or diffusion or the reaction must proceed at an interface between the
reactants. If the reaction product forms a protective layer, the reaction may stop unless enough agitation is present to break up the reactant particles and expose fresh surface. The reaction itself may produce enough agitation to do this, or the conditions under which the reaction takes place may do this. In some cases, one of the reactants (say water) may vaporize and form a low density (and presumably slow reaction rate) layer adjacent to the surface of the other reactants. A fundamental investigation of these numerous and intricate mechanisms is probably too time-consuming to attempt at this time, but various empirical factors may be selected for study.

The following factors may be expected to affect the reaction rates:

(i) State of aggregation of reactants and products.
(ii) For solid and liquid reactants, the degree of subdivision of the reactants.
(iii) The intimacy of mixing of the reactants.
(iv) The degree of agitation, and the effect of turbulence on the process.
(v) The effect of catalysis or poisoning on the reaction by impurity atoms or additives.
(vi) The effect of protective films produced by the reaction (Alumina produced in the liquid Al, H_2O reaction).
(vii) Scale (size) effects.

This list is probably not complete. Some of the effects may be understandable on a chemical basis. The results of the Aluminum Company of America and the Aerojet Engineering Corporation (Ref. 1 to 5) on the liquid aluminum-water reaction indicate that sodium and mercury additives accelerate the rate by a chemical side reaction which de-stabilizes the protective alumina film formed on the aluminum droplets as the reaction proceeds.

The scale effect is the most troublesome. There is a general belief held by many explosive technologists that any exothermic reaction can reach explosive rates if conducted on a large scale or if it is properly initiated.
is clearly difficult under this assumption. However, discovery of suitable inhibitors or poisons, active on a microscopic scale, would give a certain degree of confidence. Furthermore, if the required scale or initiation could be quantitatively established, reactor design could be arranged to stay within a safe regime. It would be particularly helpful if a correlation between catalytic additives and the effect of scale on uncatalyzed reactions could be established. This would make it possible to estimate possible large scale behavior from small scale experiments.

**TRANSIENT HEAT TRANSFER**

There is a large body of experience relating to heat transfer under steady state conditions. The importance of similarity laws in the correlation of this information is well known.

There is a very minor amount of information available concerning heat transfer under transient conditions, particularly when an exponentially increasing heat source is present. An exploratory study should be carried out, with particular attention given to the discovery of possible similarity laws and novel, unsuspected, phenomena.

If conduction through a solid is the only important process, then the dimensionless parameter which governs the process is simply:

\[
\frac{\Delta T}{L^2}
\]

where D is the thermal diffusivity, T is the exponential time scale, and L is a linear measure of the size of the body heated by a point source.

However, if heat transfer from a solid to a liquid is important, the boiling point and enthalpy of vaporization of the liquid, the conductivity of the liquid and its vapor all enter. The problem is quite complex and will require exploratory investigation. A schematic calculation for a problem of this type is indicated in NAA-SR-31. However, the reliability of this computation is not known. The existence of a yet unknown physical process (for steady state fluid flows, turbulence represents such a process and changes the flow pattern radically from the pattern predicted by analytic laminar flow considerations) may vitiate the simple analytic scheme which has been employed.
DESIURABLE EXPERIMENTAL STUDIES

As a first step of a more complete study it is desirable to study the reaction of various liquid metals with water.

The aluminum-water reaction has already been studied, and an accelerating effect of Na, Hg, Fe₂O₃ has been found. Although additional study would no doubt be useful, it is suggested that liquid U-water, liquid Zr-water, and liquid U-Al-water reactions should be studied on a small scale and the effect of various additives, suspected of being accelerators or poisons for the reaction, should be determined. Once the effect of additives is known, purity requirements can be set and the effects of agitation and subdivision in small scale experiments determined. Investigation of the effect of large scale reactions should be postponed until a later time.

The experiments should probably be conducted in a sequence:

(a) Can the reaction reach explosive rates under optimum conditions? (This may be tested by powdered metals in water set off by a booster).

(b) Can the reaction reach explosive rates under conditions resembling reactor runaway conditions? (The possibilities here are more complex).

(c) Ultimately - what are the conditions that promote or suppress explosive behavior?

After achieving state (b), the question of scale effect will enter and at the time of this writing the answer to this question is not known. As experience is gained, perhaps suitable methods to answer the question of the effect of large scale reactions by inexpensive experiments may be found.

Experimental methods are:

(1) Initiating explosion with auxiliary explosive charge.

(2) Induction heating of metal in contact with water.

(3) Mixing of molten metal with water in a bomb calorimeter, the metal to be melted electrically, by resistance heating or by induction.

(4) Spraying of molten metal into water.
The methods of testing the extent of reaction are:

(1) Analysis of the water.
(2) Analysis of the gas formed.
(3) Analysis of precipitates formed.
(4) Pressure and temperature rise determination.
(5) Energy release determination.

At first, the following metals will be investigated.

(1) Zirconium.
(2) Uranium.
(3) Uranium-Aluminum alloys.

The reason for investigating transient heat transfer is to determine whether or not the rather straightforward analytic schemes for treating this problem are applicable or whether some novel phenomena are encountered. There are some indications in the literature that at high rates of heating the specific heat is abnormally low and phase transitions are postponed until very high degrees of superheat are obtained. In addition, peculiar mechanical effects may be encountered since the fluid flow and heat flow processes will not be in step with one another. It is suggested that a glass cell be set up and observed by means of a moving picture camera of sufficiently high speed. A ribbon of aluminum or copper may be heated electrically or inductively with an exponential time schedule, and the growth of the vapor film, power consumption for a given temperature-time schedule of the ribbon (this gives the heat transfer) determined. The visual observation should be particularly helpful in detecting novel features of the process.
REFERENCES


APPENDIX

THE FREE ENERGIES OF REACTION
OF POSSIBLE REACTOR COMPONENTS

By: W. C. Ruebsamen and H. Pearlman

The free energies of reaction of reactor materials with one another under possible runaway conditions have been calculated at temperatures ranging from 298 to 1500° K. The data are shown in the accompanying graphs. When high temperature data was not available, the equation

$$
\Delta F_T = \Delta H_{298} - T \Delta S_{298}
$$

was used.

The reactions were divided into the following groups:

A. Metal – Fluoride reactions

1. \(4 \text{Fe} + 3\text{UF}_4 = 4\text{FeF}_3 + 3\text{U}\)  
   (doesn't go)

2. \(4\text{Cr} + 3\text{UF}_4 = 4\text{CrF}_3 + 3\text{U}\)

3. \(2\text{M}_{\text{I}} + \text{UF}_4 = 2\text{MIF}_2 + \text{U}\)

4. \(\text{Na} + \text{KF} = \text{NaF} + \text{K}\)

5. \(2\text{Na} + \text{BeF}_2 = 2\text{NaF} + \text{Be}\)

6. \(4\text{Na} + \text{UF}_4 = 4\text{NaF} + \text{U}\)

7. \(2\text{Hg} + \text{UF}_4 = 2\text{HgF}_2 + \text{U}\)  
   (doesn't go)

B. Metal – water Reactions

8. \(\text{M}_{\text{I}} + \text{H}_2\text{O} = \text{M}_{\text{I}0} + \text{H}_2\)

9. \(\text{U} + 3\text{H}_2\text{O} = \text{UO}_3 + 3\text{H}_2\)

10. \(\text{U} + 2\text{H}_2\text{O} = \text{UO}_2 + 2\text{H}_2\)

11. \(2\text{Al} + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2\)

12. \(\text{Be} + \text{H}_2\text{O} = \text{BeO} + \text{H}_2\)
13. \( \text{Mg} + \text{H}_2\text{O} = \text{MgO} + \text{H}_2 \)

14. \( \text{Zr} + 2\text{H}_2\text{O} = \text{ZrO}_2 + 2\text{H}_2 \)

15. \( 2\text{Na} + \text{H}_2\text{O} = \text{Na}_2\text{O} + \text{H}_2 \)

C. Metal - Oxygen Reaction

16. \( 2\text{Be} + \text{O}_2 = 2\text{BeO} \)

D. Miscellaneous Reactions

17. \( \text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2 \)

18. \( \text{C} + \text{O}_2 = \text{CO}_2 \)

19. \( 3\text{Na} + \text{Hg} = \text{Na}_3\text{Hg}, \quad \Delta H_{298} = -112\text{ Kcal} \)

20. \( \text{Na} + \text{Hg} = \text{HgNa}, \quad \Delta H_{298} = -102\text{ Kcal} \)

21. \( \text{C} + 2\text{N}_2 = \text{CN}_4, \quad \Delta H_{298} = +92.6\text{ Kcal} \)

Of the metal-fluoride reactions, 1, 2, 3, and 7 do not take place in the temperature region studied. The reaction between Na and KF has the low free energy decrease of about 2 Kcal, and hence has very little tendency to take place. The free energy of the reaction between Na and UF\(_4\) was calculated both by using high temperature data and by using the equation \( \Delta F = \Delta H_{298} - T \Delta S_{298} \). The good agreement between the two methods gives confidence in other calculations where high temperature data was not available.

With the metal-water reactions, all of those studied, except the nickel-water reaction, will occur in the temperature region studied. The reaction with water in order of decreasing reaction tendency per mol of metal is as follows at 1000°C: Zr, U + 2H\(_2\)O, Al, U + 3H\(_2\)O, Be, Mg, Na. If liquid water is used instead of gaseous water in the U + 2H\(_2\)O reaction, the \( -\Delta F \) is about 4 Kcal less, while with the 2Na + H\(_2\)O reaction, the same substitution reduces \( -\Delta F \) by about 1 Kcal. These calculations show that little difference in \( -\Delta F \) is caused, whether liquid or gaseous water is used for the reactions.
\frac{1}{4}[4Fe + 3UF_4 = 4FeF_2 + 3U]

\frac{1}{2}[2HF + UF_4 = 2HF_2 + U]

\frac{1}{2}[2N_1 + UF_4 = 2NF_2 + U]