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FUSED SALTS AS THERMONUCLEAR
REACTOR BREEDER BLANKETS

by

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D. M. Gruen

Certain thermonuclear reactors⁽¹⁾ may use a fuel consisting of a 50-50 mixture of deuterium and tritium. To produce power economically, the reaction neutrons must be utilized for tritium production in a blanket containing lithium-6. Since substantial amounts of power will be developed in such fertile blankets (about 5 Mwd/gm-atom of tritium produced), liquid systems are of interest because of their ability to remove heat readily.⁽²⁾ For a variety of reasons which will not be discussed here, fused salts of lithium offer one of the better compromises for liquid breeder blankets. In particular, fused LiNO_2 , LiNO_3 , and slurries of Li_2O in either LiNO_2 or LiNO_3 have been thought to be particularly attractive.⁽³⁾

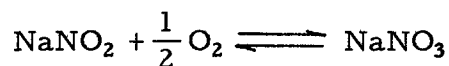
The present discussion will limit itself to a few elementary considerations regarding the chemical and physicochemical characteristics of such systems.

Although nitrates and nitrites have been studied for many years, pertinent information about the lithium salts is virtually nonexistent. The studies that will be discussed here concern themselves with some properties of alkali metal nitrates and nitrites. These studies should, of course, be extended and supplemented by studies on the corresponding lithium salts to allow a proper evaluation of the utility of the lithium salts to be made.

1. Thermal Stability

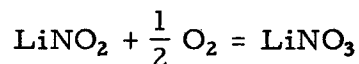
The thermal decompositions of NH_4NO_3 ⁽⁴⁾ NaNO_3 ,^(5,6) NaNO_2 ,^(5,6) KNO_3 ,⁽⁶⁾ and KNO_2 ⁽⁶⁾ have been studied. Only a few of many studies of this sort are referred to, principally to indicate the lack of agreement still existing in this field. Thus Lux⁽⁶⁾ maintained that, with NaNO_3 and KNO_3 above 550°C , the gaseous products of decomposition consisted of O_2 and NO while Freeman,⁽⁵⁾ employing mass spectrometric measurements, found O_2 as the only gas on heating NaNO_3 to 650°C . Heating to higher temperatures results in the formation of N_2 gas, but even at 780°C Freeman observed only very small amounts of nitrogen oxides. Freeman also investigated the decomposition of NaNO_2 in stainless steel between 650°C to 780°C and found the decomposition gases to consist of N_2 and O_2 . When this reaction was carried out in a platinum crucible, traces of NO and/or NO_2 were also observed. This would point to a catalytic effect influencing the mechanism and products of decomposition.

The products of decomposition in the liquid phase (oxide, peroxide, nitrite, etc.) are in equilibrium with the gaseous products. In particular, the rate of the reaction



has been studied by Freeman.

A detailed knowledge of all the products of thermal decomposition, indeed a complete understanding of the thermodynamics, particularly of the systems Li_2O , LiOH , LiNO_2 , LiNO_3 , H_2O , O_2 , N_2 , NO , and NO_2 , is necessary. The reaction



has been studied⁽⁷⁾ and has led to the value 25.1 kcal per mole for the heat of formation of LiNO_3 from $\text{LiNO}_2 + \text{O}_2$.

It is almost certain that in the presence of appreciable concentrations of NO or NO_2 in the gas phase LiNO_3 will be the stable liquid phase. More will be said about this in sections 4 and 5.

2. Neutron Damage

Neutrons, ultraviolet light, α rays, and X rays have been shown to produce nitrite and oxygen in crystals of NaNO_3 and KNO_3 .^(8,9) Studies of γ irradiation of aqueous nitrate solutions show that nitrite is produced.⁽¹⁰⁾ However, no studies of radiation damage in fused nitrates or nitrites appear to have been made. In the intense neutron flux of a thermonuclear reactor extensive radiation decomposition will undoubtedly occur. The extent and nature of this decomposition is difficult to predict, since damage will result, not only from collisions with neutrons, but also from the fragments of the fissioning lithium-6. The study of this question and of the thermodynamics of the system obviously will have to go hand in hand.

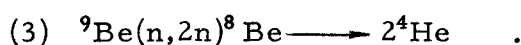
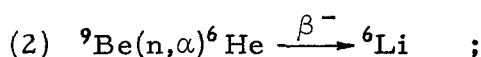
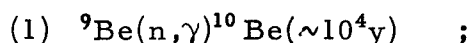
There is the additional question of the effect of neutrons on the gaseous products of decomposition and, indeed, on any gaseous atmosphere maintained over the liquid phase. As pointed out by Primak and Fuchs,⁽¹¹⁾ nitrogen can be fixed in a nuclear reactor. If the products of thermal and radiation decomposition of LiNO_2 or LiNO_3 are N_2 and O_2 , a certain amount of NO would be formed. It will be important to find out to what extent this reaction goes. In this connection, the solubility of O_2 , N_2 , NO , and NO_2 in the liquid phase will be an important parameter since the energy of the fission fragments will be available for nitrogen fixation in the liquid.

It is clear that if the products of radiation decomposition of the fused salt are O_2 and N_2 and if nitrogen fixation, either in the gas or the liquid

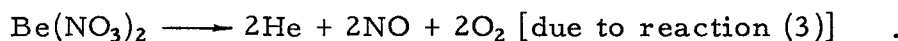
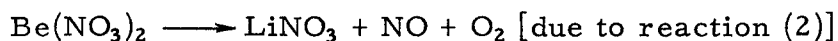
phase, is not extensive, then auxiliary nitrogen-fixation facilities would be required. The effect of this additional chemical step on the economics of nitrate blankets remains to be evaluated.

3. Neutron Multiplication

For efficient breeding of tritium, a neutron multiplication scheme must be employed. One suggested possibility consists of the addition of beryllium-9 to the blanket. The relevant nuclear reactions are



Reactions (2) and (3) will be the predominant ones with high-energy neutrons. Addition of $\text{Be}(\text{NO}_3)_2$ to the blanket to produce neutron multiplication poses certain chemical problems arising solely from nuclear transformations of beryllium. Nuclear reactions (2) and (3) are equivalent to chemical reductions. The net chemical reactions that are most likely to occur as a result are:

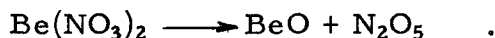


If a beryllium compound were added to the moderator instead of to the blanket, reaction (2) would act as a sink for neutrons in two ways. Energetic neutrons would be lost by the reaction itself, while thermal neutrons would be lost due to absorption by lithium-6 produced in the moderator. The neutron-breeding efficiency of beryllium would, therefore, depend somewhat on whether beryllium were incorporated into the blanket or the moderator.

Additional problems of corrosion and radiation decomposition would arise for beryllium salts added, for example, to a water moderator. In case beryllium were to be incorporated in the blanket, it can be seen from a consideration of equations (1), (2), and (3) that, to maintain a constant ratio of lithium to beryllium, it would be necessary merely to add a beryllium salt at a constant rate. No metal contamination of the system would result from burnout of beryllium.

However, various questions relating to the thermal stability and radiation damage of $\text{Be}(\text{NO}_3)_2$ would have to be considered. Some of the alkaline earth nitrates, for example $\text{Ca}(\text{NO}_3)_2$, are quite stable thermally and can be melted without decomposition. The change in chemical binding energy in going from calcium to beryllium is, however, too large to enable extrapolations of chemical or physical properties to be made.

For example, one study⁽¹²⁾ of the thermal decomposition of $\text{Be}(\text{NO}_3)_2$ indicates that decomposition of this salt begins at 170°C . The reaction was formulated by these workers as:



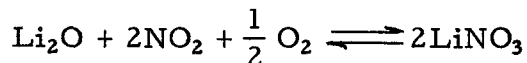
A thorough study of this system is required, as well as of solutions of $\text{Be}(\text{NO}_3)_2$ in fused $\text{Li}(\text{NO}_3)$.

The melting point of the salt mixture will depend on the concentration of beryllium salts to be added. A low melting point is obviously desirable (LiNO_2 - 232°C , LiNO_3 - 255°C) and it will be important to know the change in melting point as a function of concentration of beryllium salt. Binary salt mixtures of this sort often have eutectic compositions, so that in the most favorable case a marked depression in the melting point of the pure components could arise. Complete phase diagrams would have to be worked out in any case. If one were not working at a eutectic composition, phase separation might occur on solidification of the mixture. This would be especially true if there were no extensive regions of solid solution.

If the densities of the two components were quite different, density gradients would be established. Thus, unless proper mixing were provided, concentration gradients would lead to inhomogeneous neutron, and therefore energy, production in the blanket. This problem merits serious consideration.

4. Slurries of Li_2O in LiNO_2 and LiNO_3

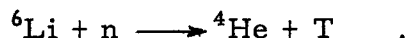
The use of Li_2O slurries in LiNO_2 and LiNO_3 was suggested⁽³⁾ principally because in this way one could obtain higher atom densities of Li. It turns out that Li_2O has a density about 50% greater than that of Li metal. As implied in the present report, a nitrite or nitrate system will probably have to be operated in the presence of considerable nitrogen oxide pressure to prevent decomposition. The equilibrium



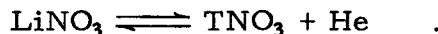
may lie very far to the right. If this situation prevailed, slurry would be converted to pure fused salt at the expense of NO_2 and O_2 . In other words, Li_2O slurries in LiNO_2 or LiNO_3 would be thermodynamically unstable in the presence of NO , NO_2 , and O_2 . Slurries of Li_2O in LiNO_2 might still be used in the absence of nitrogen oxides. In this case, thermal and radiation decomposition would result in the continuous transformation of LiNO_2 into Li_2O , necessitating continuous additions of fresh LiNO_2 .

5. Tritium Holdup

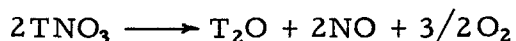
The production of tritium results from the nuclear reaction



The net chemical changes occurring in the fused salt as a result of this nuclear reaction alone may be formally written as:



It is likely, however, that in the melt the further reaction



would occur. Tritium holdup in the blanket would then depend very strongly on the solubility of T_2O in the fused LiNO_3 . Some preliminary observations⁽¹³⁾ indicate that the solubility of H_2O in fused LiNO_3 is much greater than in other alkali metal nitrates, presumably because of the great polarizing power of the small lithium ion. Obviously this question deserves very careful consideration.

In the presence of substantial pressures of nitrogen oxides, species such as LiOT would be expected to be relatively unstable. However, in the absence of nitrogen oxides, secondary reaction products such as LiOT would be favored, especially in systems involving Li_2O . The stability of LiOT would make tritium holdup in such systems an extremely serious problem.

Finally, attention must be given to the gas phase. It is expected that the volatile tritium species will be T_2O . In the presence of nitrogen oxides, equilibria involving the formation of TNO_3 must be considered. Experiments designed to test the effects on container materials of H_2O gas in the presence of nitrogen oxides must be performed in order to assess the corrosion problems associated with this system.

6. ${}^{14}\text{C}$ Production

The production of carbon-14 through (n,p) reaction on nitrogen-14 will result in the formation of carbonate. The chemical reaction is



Lithium carbonate is quite a stable substance. It does not decompose appreciably below 600°C . However, the stability of carbonate in the presence of nitrate is not known. It is conceivable that appreciable concentrations of carbonate could be built up in the melt. Decomposition would lead to the formation of CO_2 in the gas phase, which could be scavenged out of the gas stream.

7. Corrosion

Stainless steel is apparently not attacked by nitrates, even at 600-700°C. However, the corrosion problems associated with Li_2O and LiOT in the melt, as well as with T_2O and TNO_3 in the melt and in the gas phase, must be explored. There is the additional problem of electrolytic potentials which may be set up in the melt. Highly reactive metallic species might be formed. Such species would be expected to have very short lifetimes in the nitrate medium, but, if they occurred at the melt-metal interface, their corrosion effects might nevertheless be appreciable. The unknown factor of the effect of the radiation field on corrosion remains to be studied.

8. Conclusion

The present discussion envisages fused LiNO_3 as a breeder blanket for a thermonuclear reactor. This salt would be pumped in closed containers pressurized with nitrogen oxide gases. The radiation field is expected to aid in maintaining chemical equilibrium. Under the conditions envisaged, LiNO_3 would be the thermodynamically stable condensed phase. Carbonate and triton ions would accumulate to some extent in the melt. Tritium would end up in the gas phase as T_2O and could be removed as such from the gas phase. Tritium holdup in the melt would depend on a multitude of factors which cannot as yet be evaluated for lack of experimental data. It has been assumed throughout the discussion that the chemical equilibria tending to reverse the effects of radiation decomposition would be fast compared with the radiation decomposition rate. The validity of this assumption can only be proved or disproved by experiment. The rate determining step will probably be diffusion controlled, i.e., the rate of diffusion of nitrogen oxides into the melt. The first experiment that is planned, therefore, is a study of the γ -ray-induced decomposition of LiNO_3 in the presence and absence of nitrogen oxides.

Acknowledgement

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