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Calculation of Reaction Energies and Adiabatic Temperatures for Waste Tank Reactions

L. L. Burger

October 1995

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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MASTER

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Summary

Continual concern has been expressed over potentially hazardous exothermic reactions that might occur in Hanford Site underground waste storage tanks. These tanks contain many different oxidizable compounds covering a wide range of concentrations. Several compounds may be in concentrations and quantities great enough to be considered a hazard in that they could undergo rapid and energetic chemical reactions with nitrate and nitrite salts that are present it heated to the initiating or critical temperature. The chemical hazards are a function of several interrelated factors, including the amount of energy (heat) produced, how fast it is produced, and the thermal absorption and heat transfer properties of the system. The reaction path(s) will determine the amount of energy produced and kinetics will determine the rate that it is produced. The tanks also contain many inorganic compounds inert to oxidation. These compounds act as diluents and can inhibit exothermic reactions because of their heat capacity and thus, in contrast to the oxidizable compounds, provide mitigation of hazardous reactions.

In this report the energy that may be released when various organic and inorganic compounds react is computed as a function of the reaction-mix composition and the temperature. The enthalpy, or integrated heat capacity, of these compounds and various reaction products is presented as a function of temperature; the enthalpy of a given mixture can then be equated to the energy release from various reactions to predict the maximum temperature which may be reached. This is estimated for several different compositions. Alternatively, the amounts of various diluents required to prevent the temperature from reaching a critical value can be estimated. Reactions taking different paths, forming different products such as N_2O in place of N_2 are also considered, as are reactions where an excess of caustic is present. Oxidants other than nitrate and nitrite are considered briefly.

The relative available energy per unit mass of the various oxidizable compounds, or "fuels," that may be present ranges from 1 to about 25. Stoichiometric mixes with oxidant, e.g., fuel plus the required amount of sodium nitrate ($NaNO_3$) for a complete reaction, compared on a mass basis, also show large differences. This "energy density" covers a range of 1 to about 5.

A consequence of different stoichiometries for different fuels is that an excess of sodium nitrate or nitrite for one reactant may be a deficiency for another. This is significant since excess nitrate or nitrite is an excellent heat sink, especially at elevated temperatures.

The efficiency of various compounds as heat sinks, i.e., their enthalpies, vary greatly. In the wastes water is the most significant material at temperatures up to slightly above $100^\circ C$. From $100^\circ C$ to about $300^\circ C$ the greatest effect is probably from hydrated salts, with some contribution from concentrated caustic solutions. The loss of water from these materials requires a large energy input, some 50% to 100% greater than for vaporization of the same quantity of pure water. These hydrated materials are expected to play an important role in limiting the temperature rise, should an exothermic reaction begin in the 200° to $300^\circ C$ range. From about $300^\circ C$ to about $700^\circ C$, solid phase changes and melting phenomena are major heat sinks. Above about $700^\circ C$, decomposition of inorganic

compounds becomes very important, accompanied by volatilization of several materials. These latter steps require large amounts of energy. In addition to these processes, the normal increase in heat capacity with temperature, for pure compounds, is also significant.

Stoichiometric mixtures theoretically can produce very high temperatures, about 1900°C to 2000°C is calculated for a mixture of sodium nickel ferrocyanide ($\text{Na}_2\text{NiFe}(\text{CN})_6$) and NaNO_3 . This is not surprising since such mixtures may undergo deflagrations if heated to above about 300°C. A similar mix with sodium acetate (NaCH_3COO) and NaNO_3 would produce a maximum temperature about 200°C lower but as indicated in the literature could also deflagrate if heated to above 350°C. However, dilution with inert materials such as an aqueous solution, hydrated sodium aluminate, excess nitrate, etc., can easily drop the maximum adiabatic temperature to a few hundred degrees, or even prevent propagation of the reaction completely. No attempt is made to predict the severity of a given potential exothermic reaction. Rather, the goal is to calculate the theoretical energy release for a given reaction path. In this report, data are presented in tabular and graphic form to permit easy calculation of these and related quantities. Also included are data on the total gas formation from the various reactions. This quantity, including steam formation from excess water, may be important in a safety evaluation.

Because of the very large effective heat capacity of typical waste-tank constituents at the higher temperatures, it would not be expected that reaction mixtures would reach temperatures required for aerosol formation by massive vaporization of metal compounds. An exception may be cesium, as the vapor pressure of CsOH is calculated to be about 0.5 atm at 950°C. However, it is predicted that the actual volatility will be determined by the $\text{H}_2\text{O}/\text{CO}_2$ ratio, and a small amount of CO_2 could prevent vaporization since the carbonate (non-volatile) is more stable than the hydroxide. It is probable that only experimental work can answer this question.

If reactions follow a higher energy path, e.g., lead to kinetically stable intermediates, the energy release is, of course, much lower. Low-temperature reactions tend to favor this. The oxidation reactions of compounds expected in waste tanks generally will occur stepwise and thus produce such species. Even the very fast oxidation of ferrocyanides by nitrates or nitrites occurs in three or more steps.

Experimental investigation of the oxidation mechanisms, including reaction kinetics, may determine the significant species and the critical reactions, and thus determine whether a potentially reactive waste form is hazardous from the point of view of exothermic reactions, under what conditions, and how it can be converted to a safe form.

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1.0 Introduction

Underground waste tanks at Hanford contain oxidizable compounds in concentrations and quantities that when heated to above 200°C may be great enough to undergo rapid and energetic chemical reactions with nitrate and nitrite salts that are present. It is important to know what energy can be released with the different compounds. It is also important to know how much excess salts, inert solids, or water is required, by virtue of their heat capacities, to prevent the temperature, should a reaction start, from reaching a certain value, e.g., a minimal propagation temperature. An inverse of this question is what concentration of a given oxidizable material would be required to raise the temperature to a level where the reaction rate would produce unacceptable consequences.

Experimental determination of energy releases and general thermal behavior as a function of temperature has been reported by Scheele et al. (1995), Fauske (1992), Fauske and Cash (1994), and Fauske (1995). Using thermal analysis they compared simulated organic waste with nitrate and nitrite mixtures containing model organic compounds.

In the present report we present the calculated energy evolved when various organic compounds and cyanides that may exist in the waste tanks react with nitrate or nitrite salts. Calculations are made for the maximum energy release and also for reactions which take alternate paths with different end-products. Also calculated is the enthalpy as a function of temperature for various compounds that may be present in the waste tanks and for their potential reaction products. The effect of forming different products such as N_2O instead of N_2 is also considered, as is the effect of excess caustic. From these data we may then predict what the adiabatic temperature rise would be for various oxidation reactions occurring in the different waste mixtures. Secondly, we may predict what will be the effect of concentration of both oxidants and diluents on the temperature rise. Although the report is concerned largely with nitrate and nitrite salts as oxidants, a few calculations are presented for manganese and chromium which could conceivably be present in a high oxidation state.

The focus of our investigation is primarily on low-temperature (below about 700 K) reactions that could raise existing tank temperatures and reaction rates. The greatest uncertainty in heat capacities at temperatures below about 600 K is the unknown decomposition temperatures of the various hydrates that may exist in the tanks. The energies of decomposition involved can be estimated, but the temperatures at which the decompositions occur is also very important, as is the rate of decomposition. These quantities require experimental determination. Uncertainties with respect to oxidizable material, *fuel*, include the products of reaction and the paths, i.e., the mechanisms of oxidation. The greatest uncertainty with regard to the energy released is the reaction path and the extent of oxidation occurring. For example, an organic compound may decompose and be partially lost before becoming oxidized, or the compound itself may partially or completely volatilize before reacting.

It will be seen that calculations above about 600 K become imprecise because of complex decomposition reactions, primarily of $NaNO_2$ and $NaNO_3$. The latter difficulty is not a thermodynamic issue but one that stems from the fact that the decomposition reactions are slow (Stern 1972). These reactions as well as reactions that may occur at much higher temperatures are discussed later. A similar

uncertainty is the decomposition enthalpy of the various hydrates that may exist in the tanks and the temperature range over which the decomposition occurs.

It is emphasized that the ideal oxidation reactions described here are limiting cases. In general, several complex reactions may occur with a variety of products and with less total energy evolved. For example, if nitrates or nitrites are reduced only to NO instead of N_2 , then the energy release is much less, and in some cases the reaction may become endothermic. If an organic compound is only oxidized to an intermediate instead of completely to CO_2 and H_2O , then the energy release is also less. As an example, butyl alcohol oxidized by $NaNO_3$ to CO_2 , N_2 , and H_2O releases 1973 kJ per mol. Production of N_2O in place of N_2 lowers the value to 1614 kJ; if NO is formed, 932 kJ. If the oxidation stops with sodium oxalate (still producing N_2), then the energy release is 667 kJ.

Another problem is identifying the actual compounds that may exist in the waste tanks. The various materials may exist in solution, in a crystalline salt cake, in a sludge form, and in some cases as a separate organic phase. Organic compounds that are aqueous soluble such as some ethylenediaminetetracetic acid (EDTA) complexes may get transferred to different tanks as the supernate is moved (Barney 1994). The high pH solution phase, as the tank approaches dryness, is saturated in nitrates and nitrites and contains a variety of cations including sodium, aluminum, calcium, iron, etc., individually or as complexes. Anions include sulfate, phosphate, silicates, carbonate, hydroxide, and organic species. Many of the latter may result from extensive radiolytic degradation or ambient temperature chemical reaction, such as oxidation by nitrite ion, of the originally added organic compounds. While these low-temperature solution reactions are not discussed here, some of the reaction products are included in the tables. These "aging" reactions have been discussed by many workers, Ashby and coworkers (1992, 1995), Babad et al. (1993), and Camaioni and coworkers (1994, 1995).

In predicting the high-temperature species, equilibria among the reaction products are assumed. This may be only an approximation for the fast reactions involved. It is notable, however, that residues from conventional explosive reactions contain the predicted compounds in high proportions (Ornellas 1974). The importance of reaction kinetics is discussed but no attempt is made to predict the kinetic behavior of the various reactive mixtures. It is also beyond the scope of this study to predict whether deflagrations or detonations might occur. Probably most of the organic compounds listed could be made to deflagrate if heated with nitrates or nitrites under optimal conditions. There are plenty of examples of organic compound-oxidant explosions (Stull 1977). However, as noted by Beitel (1976, 1977), many organic compounds tend to volatilize before the critical temperature is reached, unless the compounds are confined. A brief discussion of terminology is important here. "Explosion" is the term normally used to define an extremely rapid reaction producing heat and large volumes of gas, i.e., producing high pressures and temperatures. Thus it would apply to some of the many reactions considered in this report. However, there are many kinds of explosives. "Low explosives" comprise a large group which propagate by heat transfer and include propellants which produce large gas volumes but are relatively slow, pyrotechnics which produce high temperatures and hence much light with minimal gas production, and another group which includes mixtures like black powder. The latter mixtures and compounds "burn" at a very rapid rate, producing high temperatures and pressures which some authors define as a deflagration. At the other end of the scale are high explosives, either primary or secondary. Primary high explosives are normally used to ignite secondary explosives. Both of these show reactions characterized by an easy transition to detonation. In a detonation the

reaction front moves supersonically, at perhaps 1000 times the velocity of a deflagration. In contrast to low explosives which do their damage by pressure, in a detonation the energy is transferred by the high speed shock wave which propagates the reaction and at the same time literally rips rather than pushes material apart. A detonation is considered impossible in a system where there is adjacent heat absorbing material as in a Hanford waste tank. In this report we will use the term "deflagration" to make it clear we are not considering high explosives.

The reactions discussed in this report cover a wide range of rates. Some mixtures, like the ferrocyanide-nitrate or nitrite combination, react very rapidly with a high brisance (shattering power) (Scheele et al. 1992). Kozlowski and Bartholomew (1968) reported that sodium acetate at a concentration of 30 wt% exploded without warning after one hour at 623 K. Many of the others show slower rates. However, we are not primarily concerned with trying to predict the exact nature of the exothermic reactions; Any thermal excursion that would release waste or damage a tank would be a serious event. Rather, the purpose is to present the theoretical enthalpy data for various reaction paths and different environments.

Finally, it is hoped that the data presented will help to evaluate whether or not different components that may be present in Hanford wastes are actually hazardous with respect to fast exothermic reactions and to what degree; and to guide planning for resolution of tank waste-handling questions such as the following: Can the wastes be modified in-tank, perhaps through further slow reactions? Can they be removed and thermally treated under controlled conditions?

2.0 Data

Table A.1 lists the enthalpy of formation, free energies of formation, and the heat capacities of various compounds of interest. Data are taken primarily from National Bureau Standard (NBS) tables (Wagman et al. 1982), Barin (1989), and the HSC *Chemistry for Windows* (HSC 1994). Data for organic compounds are supplemented by Domalski (1972). Data for conventional explosives are from Dobratz and Crawford (1985). Heats of formation for the sodium salts of the acids—citric, EDTA, and dibutyl phosphoric—were estimated by comparing the differences between the acids and the sodium salts of the other compounds listed, such as acetic, glyoxylic, oxalic, etc., for which the enthalpy of formation is known. Comparisons were also made by combining heats of solution with enthalpies of the aqueous solutions and aqueous ions, using data from Wagman et al. (1982). A value of 235 ± 10 kJ per sodium atom was chosen. Estimated data in the tables are indicated in footnotes.

The enthalpy of formation of tributyl phosphate (TBP) is based on several different measurements. Various authors report values ranging from -1250 to -1458 kJ (Burger 1988). The recommended value is 1450 ± 150 kJ/mol. For DBP (dibutyl phosphate) the enthalpy was estimated by comparing the replacement of a butyl group with hydrogen in a number of ester alcohol pairs. The value chosen was -1500 ± 150 kJ/mol. Data for ethylenediamine tetraacetic acid (EDTA) are given by Domalski (1973). An estimate of the enthalpy of formation of hydroxyethylendiamine triacetic acid (HEDTA) was made by comparing values of several pairs of compounds where a CH_2OH group was replaced by COOH . The sodium salts were then estimated by adding -235 kJ for each sodium.

The heats of formation of the alkali nickel ferrocyanides or ferricyanides have not been reported. Based on ΔH_F data for other transition metal hexacyano iron compounds, it is estimated at $+50 \pm 60$ kJ per mol of CN. Based on numerous free-energy data for other compounds and correcting for entropy, it is estimated at $+80 \pm 80$ kJ per mol of CN. Thus, although the value is likely to be slightly positive, we have used a value of 0 for simplicity.

Enthalpy data as a function of temperature for pure compounds are tabulated in Table A.3 in the Appendix in the form $H_T - H_{333}$, where H_T is the enthalpy at the temperature T and H_{333} is the enthalpy at 333 K, the arbitrary reference temperature for this study. Values were computed for 100° intervals up to 1000 K. For several compounds data were extended to 1500 K or 1800 K. Enthalpies of solid transitions, melting, and vaporization are included. The estimation of missing data is discussed where appropriate. Where temperature-dependent data were not available from standard tables, they were calculated by integration of heat-capacity data. Data at intermediate temperatures of interest were obtained either from heat-capacity data or more commonly by numerical interpolation.

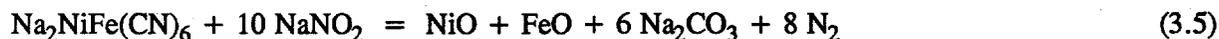
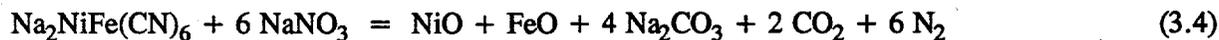
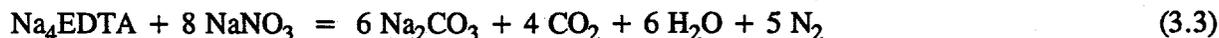
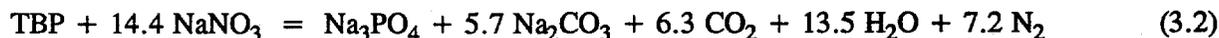
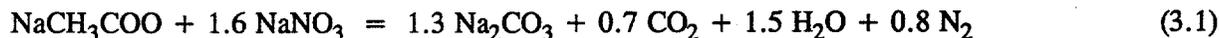
The melting point of the salt mix and the heat of fusion are important quantities, since it is not likely that a fast reaction between two components can occur with both as solids. The practical consequence of this is that the heat produced in a reaction must be much greater than the enthalpy of fusion for a fast reaction (deflagration) to occur. Several heat-capacity data are listed in Table A.2. Heat-capacity data as a function of temperature were not found for most of the organic compounds.

3.0 Calculations

The energy available for a given reaction is calculated at 298 K, using the standard enthalpies of formation listed in Table A.1. Values at other temperatures can be obtained either from heat-capacity data or more easily from enthalpy data in Table A.3.

3.1 Oxidation Reactions

The maximum energy release results when the products of reactions with nitrates and nitrites are nitrogen, Na_2CO_3 , H_2O , and CO_2 . Typical reactions involving acetates, tributyl phosphate (TBP), ethylenediamine tetraacetic acid (EDTA), and ferrocyanides as examples are



These reactions and others, and their modifications are discussed in more detail in this section. Production of oxides of nitrogen in place of nitrogen, or CO in place of CO_2 greatly lowers the energy release (Burger et al. 1991). Table 3.1 gives data for sodium acetate, and 8 other organic compounds. Here nitrate is compared to nitrite as an oxidant, as is the effect of producing N_2O in place of N_2 ; the effect of the presence of excess NaOH present is illustrated. Data for possible reactions of sodium acetate, which would produce different gaseous products, are shown in Table 3.2. Table 3.3 gives reaction enthalpies for several reactions of different cyanides, including sodium nickel ferrocyanide, at one time present in some of the waste tanks.

The effect of forming different reaction products is very pronounced, as seen from the data in Tables 3.1, 3.2, and 3.3. The actual products eventually formed, assuming equilibrium is reached, depend on the final temperature. It is recognized that with fast exothermic reactions equilibria among

Table 3.1. Enthalpy of Reaction for Typical Organic Compounds

| Compound | Reaction | ΔH , kJ/Mole | ΔH , kJ/g | ΔH , kJ/g-C |
|--|--|----------------------|-------------------|---------------------|
| Sodium Acetate (NaCH_2CO_2) | $\text{NaCH}_3\text{COO} + 1.6 \text{ NaNO}_3 \rightleftharpoons 1.3 \text{ Na}_2\text{CO}_3 + 0.7 \text{ CO}_2 + 1.5 \text{ H}_2\text{O} + 0.8 \text{ N}_2$ | -650 | -7.94 | -27.1 |
| | $\text{NaCH}_3\text{COO} + 2 \text{ NaNO}_3 \rightleftharpoons 1.5 \text{ Na}_2\text{CO}_3 + 0.5 \text{ CO}_2 + 1.5 \text{ H}_2\text{O} + \text{N}_2\text{O}$ | -530 | -6.45 | -22.0 |
| | $\text{NaCH}_3\text{COO} + 1.6 \text{ NaNO}_3 + 1.4 \text{ NaOH} \rightleftharpoons 2 \text{ Na}_2\text{CO}_3 + 2.2 \text{ H}_2\text{O} + 0.8 \text{ N}_2$ | -740 | -9.02 | -30.8 |
| | $\text{NaCH}_3\text{COO} + 2.0 \text{ NaNO}_3 + \text{NaOH} \rightleftharpoons 2 \text{ Na}_2\text{CO}_3 + 2.0 \text{ H}_2\text{O} + \text{N}_2\text{O}$ | -580 | -7.11 | -24.3 |
| | $\text{NaCH}_3\text{COO} + 2.67 \text{ NaNO}_2 \rightleftharpoons 1.83 \text{ Na}_2\text{CO}_3 + 0.17 \text{ CO}_2 + 1.5 \text{ H}_2\text{O} + 1.33 \text{ N}_2^{(e)}$ | -840 | -10.2 | -34.8 |
| | $\text{NaCH}_3\text{COO} + 4 \text{ NaNO}_2 \rightleftharpoons 2 \text{ Na}_2\text{CO}_3 + \text{NaOH} + \text{H}_2\text{O} + 2 \text{ N}_2\text{O}^{(b)}$ | -620 | -7.58 | -25.9 |
| | $\text{NaCH}_3\text{COO} + 2.667 \text{ NaNO}_2 + 0.333 \text{ NaOH} \rightleftharpoons 2 \text{ Na}_2\text{CO}_3 + 1.667 \text{ H}_2\text{O} + 1.33 \text{ N}_2^{(c)}$ | -860 | -10.5 | -35.7 |
| | $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 3.6 \text{ NaNO}_3 \rightleftharpoons 3.3 \text{ Na}_2\text{CO}_3 + 2.7 \text{ CO}_2 + 2.5 \text{ H}_2\text{O} + 1.8 \text{ N}_2$ | -1460 | -5.66 | -20.3 |
| | $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 4.5 \text{ NaNO}_3 \rightleftharpoons 3.75 \text{ Na}_2\text{CO}_3 + 2.25 \text{ CO}_2 + 2.5 \text{ H}_2\text{O} + 2.25 \text{ N}_2\text{O}$ | -1190 | -4.60 | -16.5 |
| | $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 3.6 \text{ NaNO}_3 + 5.4 \text{ NaOH} \rightleftharpoons 6 \text{ Na}_2\text{CO}_3 + 5.2 \text{ H}_2\text{O} + 1.8 \text{ N}_2$ | -1805 | -7.00 | -25.1 |
| $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 4.5 \text{ NaNO}_3 + 4.5 \text{ NaOH} \rightleftharpoons 6 \text{ Na}_2\text{CO}_3 + 4.75 \text{ H}_2\text{O} + 2.25 \text{ N}_2\text{O}$ | -1470 | -5.71 | -20.5 | |
| Sodium Citrate ($\text{Na}_3\text{C}_6\text{H}_7\text{O}_7$) | $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 6 \text{ NaNO}_2 \rightleftharpoons 4.5 \text{ Na}_2\text{CO}_3 + 1.5 \text{ CO}_2 + 2.5 \text{ H}_2\text{O} + 3 \text{ N}_2$ | -1880 | -7.28 | -26.1 |
| | $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 9 \text{ NaNO}_2 \rightleftharpoons 6 \text{ Na}_2\text{CO}_3 + 2.5 \text{ H}_2\text{O} + 4.5 \text{ N}_2\text{O}$ | -1540 | -5.96 | -21.4 |
| | $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 6 \text{ NaNO}_2 + 3 \text{ NaOH} \rightleftharpoons 6 \text{ Na}_2\text{CO}_3 + 4 \text{ H}_2\text{O} + 3 \text{ N}_2$ | -2070 | -8.02 | -28.7 |
| | $\text{Na}_4\text{C}_{10}\text{H}_{12}\text{O}_8\text{H}_{12} + 8 \text{ NaNO}_3 \rightleftharpoons 6 \text{ Na}_2\text{CO}_3 + 4 \text{ CO}_2 + 6 \text{ H}_2\text{O} + 5 \text{ N}_2$ | -3350 | -8.82 | -27.9 |
| | $\text{Na}_4\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2 + 10 \text{ NaNO}_3 \rightleftharpoons 7 \text{ Na}_2\text{CO}_3 + 3 \text{ CO}_2 + 6 \text{ H}_2\text{O} + 5 \text{ N}_2\text{O} + \text{N}_2$ | -2740 | -7.21 | -22.8 |
| | $\text{Na}_4\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2 + 8 \text{ NaNO}_3 + 8 \text{ NaOH} \rightleftharpoons 10 \text{ Na}_2\text{CO}_3 + 10 \text{ H}_2\text{O} + 5 \text{ N}_2$ | -3860 | -10.2 | -32.3 |
| | $\text{Na}_4\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2 + 10 \text{ NaNO}_3 + 6 \text{ NaOH} \rightleftharpoons 10 \text{ Na}_2\text{CO}_3 + 9 \text{ H}_2\text{O} + 5 \text{ N}_2\text{O} + \text{N}_2$ | -3130 | -8.22 | -26.0 |
| | $\text{Na}_4\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2 + 13.3 \text{ NaNO}_2 \rightleftharpoons 8.67 \text{ Na}_2\text{CO}_3 + 1.33 \text{ CO}_2 + 6 \text{ H}_2\text{O} + 7.65 \text{ N}_2$ | -4270 | -11.2 | -35.6 |
| | $\text{Na}_4\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2 + 20 \text{ NaNO}_2 \rightleftharpoons 10 \text{ Na}_2\text{CO}_3 + 4 \text{ H}_2\text{O} + 4 \text{ NaOH} + 10 \text{ N}_2\text{O} + \text{N}_2$ | -2980 | -7.83 | -24.8 |
| | $\text{Na}_4\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2 + 13.33 \text{ NaNO}_2 + 2.667 \text{ NaOH} \rightleftharpoons 10 \text{ Na}_2\text{CO}_3 + 7.33 \text{ H}_2\text{O} + 7.667 \text{ N}_2$ | -4450 | -11.7 | -37.0 |

Table 3.1. (Contd)

| Compound | Reaction | ΔH , kJ/Mole | ΔH , kJ/g | ΔH , kJ/g-C |
|---|---|----------------------|-------------------|---------------------|
| Sodium HEDTA ($\text{Na}_3\text{C}_{10}\text{H}_{15}\text{O}_7\text{N}_2$) | $\text{Na}_3\text{C}_{10}\text{H}_{15}\text{O}_7\text{N}_2 + 8.8 \text{ NaNO}_3 \rightleftharpoons 5.9 \text{ Na}_2\text{CO}_3 + 4.1 \text{ CO}_2 + 7.5 \text{ H}_2\text{O} + 5.4 \text{ N}_2$ | -3710 | -10.8 | -30.9 |
| | $\text{Na}_3\text{C}_{10}\text{H}_{15}\text{O}_7\text{N}_2 + 11 \text{ NaNO}_3 \rightleftharpoons 7 \text{ Na}_2\text{CO}_3 + 3 \text{ CO}_2 + 7.5 \text{ H}_2\text{O} + 5.5 \text{ N}_2\text{O} + \text{N}_2$ | -3040 | -8.83 | -25.3 |
| | $\text{Na}_3\text{C}_{10}\text{H}_{15}\text{O}_7\text{N}_2 + 8.8 \text{ NaNO}_3 + 8.2 \text{ NaOH} \rightleftharpoons 10 \text{ Na}_2\text{CO}_3 + 11.6 \text{ H}_2\text{O} + 4.4 \text{ N}_2$ | -4230 | -12.3 | -35.2 |
| | $\text{Na}_3\text{C}_{10}\text{H}_{15}\text{O}_7\text{N}_2 + 11 \text{ NaNO}_3 + 6 \text{ NaOH} \rightleftharpoons 10 \text{ Na}_2\text{CO}_3 + 10.5 \text{ H}_2\text{O} + 5.5 \text{ N}_2\text{O} + \text{N}_2$ | -3420 | -9.94 | -28.5 |
| Sodium Glycolate ($\text{NaCH}_2\text{OHCOO}$) | $\text{Na}_3\text{C}_{10}\text{H}_{15}\text{O}_7\text{N}_2 + 14.667 \text{ NaNO}_2 \rightleftharpoons 8.833 \text{ Na}_2\text{CO}_3 + 1.167 \text{ CO}_2 + 7.5 \text{ H}_2\text{O} + 8.33 \text{ N}_2$ | -4730 | -13.7 | -39.3 |
| | $\text{Na}_3\text{C}_{10}\text{H}_{15}\text{O}_7\text{N}_2 + 22 \text{ NaNO}_2 \rightleftharpoons 10 \text{ Na}_2\text{CO}_3 + 5 \text{ NaOH} + 5 \text{ H}_2\text{O} + 11 \text{ N}_2\text{O} + \text{N}_2$ | -3600 | -10.5 | -30.0 |
| | $\text{Na}_3\text{C}_{10}\text{H}_{15}\text{O}_7\text{N}_2 + 14.667 \text{ NaNO}_2 + 2.33 \text{ NaOH} \rightleftharpoons 10 \text{ Na}_2\text{CO}_3 + 8.667 \text{ H}_2\text{O} + 8.33 \text{ N}_2$ | -4880 | -14.2 | -40.7 |
| | $\text{NaCH}_2\text{OHCOO} + 1.2 \text{ NaNO}_3 \rightleftharpoons 1.1 \text{ Na}_2\text{CO}_3 + 0.9 \text{ CO}_2 + 1.5 \text{ H}_2\text{O} + 0.6 \text{ N}_2$ | 498 | 5.08 | 20.7 |
| $\text{NaCH}_2\text{OHCOO} + 1.5 \text{ NaNO}_3 \rightleftharpoons 1.25 \text{ Na}_2\text{CO}_3 + 0.75 \text{ CO}_2 + 1.5 \text{ H}_2\text{O} + 0.75 \text{ N}_2\text{O}$ | 407.2 | 4.15 | 17.0 | |
| $\text{NaCH}_2\text{OHCOO} + 1.2 \text{ NaNO}_3 + 1.8 \text{ NaOH} \rightleftharpoons 2 \text{ Na}_2\text{CO}_3 + 2.4 \text{ H}_2\text{O} + 0.6 \text{ N}_2$ | 613.4 | 5.26 | 25.5 | |
| $\text{NaCH}_2\text{OHCOO} + 1.5 \text{ NaNO}_3 + 1.5 \text{ NaOH} \rightleftharpoons 2 \text{ Na}_2\text{CO}_3 + 2.25 \text{ H}_2\text{O} + 0.75 \text{ N}_2\text{O}$ | 503.0 | 5.13 | 20.9 | |
| $\text{NaCH}_2\text{OHCOO} + 2.0 \text{ NaNO}_2 \rightleftharpoons 1.5 \text{ Na}_2\text{CO}_3 + 0.5 \text{ CO}_2 + 1.5 \text{ H}_2\text{O} + \text{N}_2$ | 418.1 | 4.26 | 17.4 | |
| $\text{NaCH}_2\text{OHCOO} + 3.0 \text{ NaNO}_2 \rightleftharpoons 2.0 \text{ Na}_2\text{CO}_3 + 1.5 \text{ H}_2\text{O} + 1.5 \text{ N}_2\text{O}$ | 195.7 | 2.00 | 8.14 | |
| $\text{NaCH}_2\text{OHCOO} + 2.0 \text{ NaNO}_2 + \text{NaOH} \rightleftharpoons 2.0 \text{ Na}_2\text{CO}_3 + 2.0 \text{ H}_2\text{O} + \text{N}_2$ | 482.0 | 4.92 | 20.1 | |
| Sodium Dibutylphosphate ($\text{NaO}(\text{C}_4\text{H}_9\text{O})_2\text{PO}$) | $\text{NaO}(\text{C}_4\text{H}_9\text{O})_2\text{PO} + 9.6 \text{ NaNO}_3 \rightleftharpoons 3.8 \text{ Na}_2\text{CO}_3 + 4.2 \text{ CO}_2 + 9 \text{ H}_2\text{O} + \text{Na}_3\text{PO}_4 + 4.8 \text{ N}_2$ | 3952 | 17.0 | 41.1 |
| | $\text{NaO}(\text{C}_4\text{H}_9\text{O})_2\text{PO} + 12.0 \text{ NaNO}_3 \rightleftharpoons 5.0 \text{ Na}_2\text{CO}_3 + 3.0 \text{ CO}_2 + 9 \text{ H}_2\text{O} + \text{Na}_3\text{PO}_4 + 6.0 \text{ N}_2\text{O}$ | 3222 | 13.9 | 33.5 |
| | $\text{NaO}(\text{C}_4\text{H}_9\text{O})_2\text{PO} + 9.6 \text{ NaNO}_3 + 8.4 \text{ NaOH} \rightleftharpoons 8.0 \text{ Na}_2\text{CO}_3 + 13.2 \text{ H}_2\text{O} + \text{Na}_3\text{PO}_4 + 4.8 \text{ N}_2$ | 4489 | 19.3 | 46.7 |
| | $\text{NaO}(\text{C}_4\text{H}_9\text{O})_2\text{PO} + 12.0 \text{ NaNO}_3 + 6 \text{ NaOH} \rightleftharpoons 8.0 \text{ Na}_2\text{CO}_3 + 12.0 \text{ H}_2\text{O} + \text{Na}_3\text{PO}_4 + 6.0 \text{ N}_2\text{O}$ | 3605 | 15.5 | 37.5 |
| $\text{NaO}(\text{C}_4\text{H}_9\text{O})_2\text{PO} + 16.0 \text{ NaNO}_2 \rightleftharpoons 7 \text{ Na}_2\text{CO}_3 + \text{CO}_2 + 9 \text{ H}_2\text{O} + \text{Na}_3\text{PO}_4 + 8.0 \text{ N}_2\text{O}$ | 5066 | 21.8 | 52.7 | |
| $\text{NaO}(\text{C}_4\text{H}_9\text{O})_2\text{PO} + 16.0 \text{ NaNO}_2 + 2 \text{ NaOH} \rightleftharpoons 8 \text{ Na}_2\text{CO}_3 + 10 \text{ H}_2\text{O} + \text{Na}_3\text{PO}_4 + 8.0 \text{ N}_2$ | 4536 | 19.5 | 47.2 | |
| $\text{NaO}(\text{C}_4\text{H}_9\text{O})_2\text{PO} + 24 \text{ NaNO}_2 \rightleftharpoons 8 \text{ Na}_2\text{CO}_3 + 6 \text{ NaOH} + \text{Na}_3\text{PO}_4 + 6 \text{ H}_2\text{O} + 12 \text{ N}_2\text{O}$ | 3777 | 16.3 | 39.3 | |

Table 3.1. (Contd)

| Compound | Reaction | ΔH , kJ/Mole | ΔH , kJ/g | ΔH , kJ/g-C |
|--|--|----------------------|-------------------|---------------------|
| Sodium Butyrate ($\text{NaC}_4\text{H}_7\text{O}_2$) | $\text{NaC}_4\text{H}_7\text{O}_2 + 4 \text{NaNO}_3 \rightleftharpoons 2.5 \text{Na}_2\text{CO}_3 + 1.5 \text{CO}_2 + 3.5 \text{H}_2\text{O} + 2 \text{N}_2$ | -1615 | -14.7 | -33.7 |
| | $\text{NaC}_4\text{H}_7\text{O}_2 + 4 \text{NaNO}_3 + 3 \text{NaOH} \rightleftharpoons 4 \text{Na}_2\text{CO}_3 + 5 \text{H}_2\text{O} + 2 \text{N}_2$ | -1804 | -16.4 | -37.6 |
| | $\text{NaC}_4\text{H}_7\text{O}_2 + 5 \text{NaNO}_3 \rightleftharpoons 3 \text{Na}_2\text{CO}_3 + \text{CO}_2 + 3.5 \text{H}_2\text{O} + 2.5 \text{N}_2\text{O}$ | -1309 | -11.9 | -27.3 |
| | $\text{NaC}_4\text{H}_7\text{O}_2 + 5 \text{NaNO}_3 + 2 \text{NaOH} \rightleftharpoons 4 \text{Na}_2\text{CO}_3 + 4.5 \text{H}_2\text{O} + 2.5 \text{N}_2\text{O}$ | -1436 | -13.0 | -29.9 |
| Sodium Laurate ($\text{NaC}_{12}\text{H}_{23}\text{O}_2$) | $\text{NaC}_{12}\text{H}_{23}\text{O}_2 + 6.67 \text{NaNO}_2 \rightleftharpoons 3.83 \text{Na}_2\text{CO}_3 + 0.17 \text{CO}_2 + 3.33 \text{N}_2\text{O} + 3.5 \text{H}_2\text{O}$ | -2073 | -18.8 | -43.2 |
| | $\text{NaC}_{12}\text{H}_{23}\text{O}_2 + 6.67 \text{NaNO}_2 + 0.33 \text{NaOH} \rightleftharpoons 4 \text{Na}_2\text{CO}_3 + 3.33 \text{N}_2 + 3.667 \text{H}_2\text{O}$ | -2099 | -19.1 | -43.7 |
| | $\text{NaC}_{12}\text{H}_{23}\text{O}_2 + 10 \text{NaNO}_2 \rightleftharpoons 4 \text{Na}_2\text{CO}_3 + 3 \text{NaOH} + 2 \text{H}_2\text{O} + 5 \text{N}_2\text{O}$ | -1510 | -13.7 | -31.5 |
| | $\text{NaC}_{12}\text{H}_{23}\text{O}_2 + 13.6 \text{NaNO}_3 \rightleftharpoons 7.3 \text{Na}_2\text{CO}_3 + 4.7 \text{CO}_2 + 11.5 \text{H}_2\text{O} + 6.8 \text{N}_2$ | -5508 | -24.8 | -38.5 |
| Sodium Oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) | $\text{NaC}_{12}\text{H}_{23}\text{O}_2 + 17 \text{NaNO}_3 \rightleftharpoons 9 \text{Na}_2\text{CO}_3 + 3 \text{CO}_2 + 11.5 \text{H}_2\text{O} + 8.5 \text{N}_2\text{O}$ | -4473 | -20.1 | -31.0 |
| | $\text{NaC}_{12}\text{H}_{23}\text{O}_2 + 13.6 \text{NaNO}_3 + 9.4 \text{NaOH} \rightleftharpoons 12 \text{Na}_2\text{CO}_3 + 16.2 \text{H}_2\text{O} + 6.8 \text{N}_2$ | -6108 | -27.5 | -42.4 |
| | $\text{NaC}_{12}\text{H}_{23}\text{O}_2 + 17 \text{NaNO}_3 + 6 \text{NaOH} \rightleftharpoons 12 \text{Na}_2\text{CO}_3 + 14.5 \text{H}_2\text{O} + 8.5 \text{N}_2\text{O}$ | -4857 | -21.8 | -33.7 |
| | $\text{NaC}_{12}\text{H}_{23}\text{O}_2 + 22.667 \text{NaNO}_2 \rightleftharpoons 11.83 \text{Na}_2\text{CO}_3 + 0.17 \text{CO}_2 + 11.5 \text{H}_2\text{O} + 11.33 \text{N}_2$ | -7081 | -31.9 | -49.2 |
| Sodium Oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) | $\text{NaC}_{12}\text{H}_{23}\text{O}_2 + 34 \text{NaNO}_2 \rightleftharpoons 12 \text{Na}_2\text{CO}_3 + 11 \text{NaOH} + 6 \text{H}_2\text{O} + 17 \text{N}_2\text{O}$ | -6114 | -27.5 | -42.4 |
| | $\text{NaC}_{12}\text{H}_{23}\text{O}_2 + 22.667 \text{NaNO}_2 + 0.34 \text{NaOH} \rightleftharpoons 12 \text{Na}_2\text{CO}_3 + 11.67 \text{H}_2\text{O} + 11.33 \text{N}_2$ | -7103 | -32.1 | -43.7 |
| | $\text{NaC}_4\text{H}_7\text{O}_2 + \text{NaNO}_2 + 10 \text{NaNO}_3 \rightleftharpoons 4 \text{Na}_2\text{CO}_3 + 3 \text{NaOH} + 2 \text{H}_2\text{O} + 5 \text{N}_2\text{O}$ | -1510 | -32.0 | -49.3 |
| | $\text{Na}_2\text{C}_2\text{O}_4 + 0.4 \text{NaNO}_3 \rightleftharpoons 1.2 \text{Na}_2\text{CO}_3 + 0.8 \text{CO}_2 + 0.2 \text{N}_2$ | -166.5 | -1.24 | -6.94 |
| Sodium Oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) | $\text{Na}_2\text{C}_2\text{O}_4 + 0.4 \text{NaNO}_3 + 1.6 \text{NaOH} \rightleftharpoons 2 \text{Na}_2\text{CO}_3 + 0.2 \text{N}_2 + 0.8 \text{H}_2\text{O}$ | -268.8 | -2.01 | -11.2 |
| | $\text{Na}_2\text{C}_2\text{O}_4 + 0.5 \text{NaNO}_3 \rightleftharpoons 1.25 \text{Na}_2\text{CO}_3 + 0.75 \text{CO}_2 + 0.25 \text{N}_2\text{O}$ | -136.0 | 1.01 | 5.90 |
| | $\text{Na}_2\text{C}_2\text{O}_4 + 0.5 \text{NaNO}_3 + 1.5 \text{NaOH} \rightleftharpoons 2 \text{Na}_2\text{CO}_3 + 0.25 \text{N}_2\text{O} + 0.75 \text{H}_2\text{O}$ | -232.0 | -1.73 | -9.67 |
| | $\text{Na}_2\text{C}_2\text{O}_4 + 0.667 \text{NaNO}_2 \rightleftharpoons 1.33 \text{Na}_2\text{CO}_3 + 0.67 \text{CO}_2 + 0.33 \text{N}_2$ | -213.8 | -1.60 | -8.91 |
| Sodium Oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) | $\text{Na}_2\text{C}_2\text{O}_4 + 0.667 \text{NaNO}_2 + 1.333 \text{NaOH} \rightleftharpoons 2.0 \text{Na}_2\text{CO}_3 + \text{N}_2 + 0.657 \text{H}_2\text{O}$ | -298.2 | -2.22 | -12.4 |
| | $\text{Na}_2\text{C}_2\text{O}_4 + \text{NaNO}_2 \rightleftharpoons 1.5 \text{Na}_2\text{CO}_3 + 0.5 \text{CO}_2 + 0.5 \text{N}_2\text{O}$ | -175.2 | -1.31 | -7.32 |
| Sodium Oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) | $\text{Na}_2\text{C}_2\text{O}_4 + \text{NaNO}_2 + \text{NaOH} \rightleftharpoons 2 \text{Na}_2\text{CO}_3 + 0.5 \text{N}_2\text{O} + 0.5 \text{H}_2\text{O}$ | -239.1 | -1.78 | -9.97 |

Table 3.1. (Contd)

| Compound | Reaction | ΔH , kJ/Mole | ΔH , kJ/g | ΔH , kJ/g-C |
|---|--|----------------------|-------------------|---------------------|
| Sodium Tartrate ($\text{Na}_2(\text{CHOH})_2(\text{COO})_2$) | $\text{C}_4\text{H}_4\text{O}_6\text{Na}_2 + 2 \text{NaNO}_3 \rightleftharpoons 2 \text{Na}_2\text{CO}_3 + 2 \text{CO}_2 + 2 \text{H}_2\text{O} + \text{N}_2$ | -823 | -4.25 | -17.2 |
| | $\text{C}_4\text{H}_4\text{O}_6\text{Na}_2 + 2 \text{NaNO}_3 + 4 \text{NaOH} \rightleftharpoons 4 \text{Na}_2\text{CO}_3 + 4 \text{H}_2\text{O} + \text{N}_2$ | -1076 | -5.54 | -22.4 |
| | $\text{C}_4\text{H}_4\text{O}_6\text{Na}_2 + 2.5 \text{NaNO}_3 \rightleftharpoons 2.25 \text{Na}_2\text{CO}_3 + 1.75 \text{CO}_2 + 2 \text{H}_2\text{O} + 1.25 \text{N}_2$ | -670 | -3.45 | -17.0 |
| | $\text{C}_4\text{H}_4\text{O}_6\text{Na}_2 + 2.5 \text{NaNO}_3 + 3.5 \text{NaOH} \rightleftharpoons 4 \text{Na}_2\text{CO}_3 + 3.75 \text{H}_2\text{O} + 1.25 \text{N}_2$ | -892 | -4.60 | -18.6 |
| Sodium Formate (NaCHOO) | $\text{C}_4\text{H}_4\text{O}_6\text{Na}_2 + 3.33 \text{NaNO}_2 \rightleftharpoons 2.667 \text{Na}_2\text{CO}_3 + 1.3 \text{CO}_2 + 2 \text{H}_2\text{O} + 1.667 \text{N}_2$ | -1055 | -5.44 | -22.0 |
| | $\text{C}_4\text{H}_4\text{O}_6\text{Na}_2 + 3.33 \text{NaNO}_2 + 2.667 \text{NaOH} \rightleftharpoons 4 \text{Na}_2\text{CO}_3 + 3.337 \text{H}_2\text{O} + 1.667 \text{N}_2$ | -860 | -4.43 | -17.9 |
| | $\text{C}_4\text{H}_4\text{O}_6\text{Na}_2 + 5 \text{NaNO}_2 \rightleftharpoons 3.5 \text{Na}_2\text{CO}_3 + 0.5 \text{CO}_2 + 2 \text{H}_2\text{O} + 2.5 \text{N}_2$ | -868.8 | -4.48 | -18.1 |
| | $\text{C}_4\text{H}_4\text{O}_6\text{Na}_2 + 5 \text{NaNO}_2 + \text{NaOH} \rightleftharpoons 4 \text{Na}_2\text{CO}_3 + 2.5 \text{H}_2\text{O} + 2.5 \text{N}_2\text{O}$ | -933 | -4.80 | -19.5 |
| Sodium Formate (NaCHOO) | $\text{NaCHOO} + 0.4 \text{NaNO}_3 \rightleftharpoons 0.7 \text{Na}_2\text{CO}_3 + 0.3 \text{CO}_2 + 0.5 \text{H}_2\text{O} + 0.2 \text{N}_2$ | -176.3 | -2.59 | -14.7 |
| | $\text{NaCHOO} + 0.4 \text{NaNO}_3 + 0.6 \text{NaOH} \rightleftharpoons \text{Na}_2\text{CO}_3 + 0.8 \text{H}_2\text{O} + 0.2 \text{N}_2$ | -214.3 | -3.15 | -17.9 |
| | $\text{NaCHOO} + 0.5 \text{NaNO}_3 \rightleftharpoons 0.75 \text{Na}_2\text{CO}_3 + 0.25 \text{CO}_2 + 0.25 \text{N}_2\text{O} + 0.5 \text{H}_2\text{O}$ | -146.4 | -2.15 | -12.2 |
| | $\text{NaCHOO} + 0.5 \text{NaNO}_3 + 0.5 \text{NaOH} \rightleftharpoons \text{Na}_2\text{CO}_3 + 0.25 \text{N}_2\text{O} + 0.75 \text{H}_2\text{O}$ | -178.3 | -2.62 | -14.9 |
| Sodium Formate (NaCHOO) | $\text{NaCHOO} + 1.667 \text{NaNO}_2 \rightleftharpoons 0.833 \text{Na}_2\text{CO}_3 + 0.167 \text{CO}_2 + 0.5 \text{H}_2\text{O} + 0.33 \text{N}_2$ | -223.2 | -3.28 | -18.6 |
| | $\text{NaCHOO} + 0.667 \text{NaNO}_2 + 0.33 \text{NaOH} \rightleftharpoons \text{Na}_2\text{CO}_3 + 0.667 \text{H}_2\text{O} + 0.33 \text{N}_2$ | -243.9 | -3.58 | 20.3 |
| | $\text{NaCHOO} + 1.667 \text{NaNO}_2 \rightleftharpoons \text{Na}_2\text{CO}_3 + 0.5 \text{N}_2\text{O} + 0.5 \text{H}_2\text{O}$ | -184.9 | -2.72 | -15.4 |

Table 3.2. Reactions of Sodium Acetate

| Reactants, Mols | | | Products, Mols ^(a) | | | | | | | | | | $-\Delta H_{Rx}$, KJ | | | |
|---------------------|------------------|-------|---------------------------------|-----------------|------------------|----------------|------------------|------|-----------------|------|-----|---|-----------------------|---|---|-----|
| Oxidant | H ₂ O | NaOH | Na ₂ CO ₃ | CO ₂ | H ₂ O | N ₂ | N ₂ O | NO | NH ₃ | NaOH | CO | Na ₂ C ₂ O ₄ | | | | |
| NaNO ₃ | | | | | | | | | | | | | | | | |
| 1.6 | - | - | 1.3 | 0.70 | 1.50 | 0.80 | - | - | - | - | - | - | - | - | - | 651 |
| 2.0 | - | - | 1.5 | 0.50 | 1.50 | - | 1.00 | - | - | - | - | - | - | - | - | 529 |
| 2.00 | - | 1.00 | 2.00 | - | 2.00 | - | 1.00 | - | - | - | - | - | - | - | - | 583 |
| 1.60 | - | 1.40 | 2.00 | - | 2.20 | 0.8 | - | - | - | - | - | - | - | - | - | 740 |
| 2.67 | - | - | 1.833 | 0.167 | 1.50 | - | - | 2.67 | - | - | - | - | - | - | - | 304 |
| 2.67 | - | 0.333 | 2.00 | - | 1.667 | - | - | 2.67 | - | - | - | - | - | - | - | 324 |
| 1.00 | - | - | 1.00 | 1.00 | - | - | - | - | 1.00 | - | - | - | - | - | - | 394 |
| 1.00 | - | 2.00 | 2.00 | - | 1.00 | - | - | - | 1.00 | - | - | - | - | - | - | 522 |
| 0.80 | - | - | - | - | - | - | - | - | - | - | 2.0 | - | - | - | - | 49 |
| 1.20 | - | - | - | - | 1.40 | 0.60 | - | - | - | 0.20 | - | 1.00 | - | - | - | 472 |
| 1.60 ^(b) | - | - | - | 2.00 | 0.20 | 0.80 | - | - | - | 2.60 | - | - | - | - | - | 485 |
| 2.00 ^(b) | - | - | - | 2.00 | - | - | 1.00 | - | - | 3.00 | - | - | - | - | - | 337 |
| 1.60 ^(b) | - | - | 2.00 | 2.00 | 1.20 | 0.80 | - | - | - | 1.60 | - | - | - | - | - | 525 |
| NaNO ₂ | | | | | | | | | | | | | | | | |
| 2.666 | - | - | 1.833 | 0.17 | 1.50 | 1.333 | - | - | - | - | - | - | - | - | - | 836 |
| 2.666 | - | 0.333 | 2.00 | - | 1.667 | 1.333 | - | - | - | - | - | - | - | - | - | 858 |
| 4.00 | - | - | 2.00 | - | - | - | 2.00 | - | - | 1.00 | - | - | - | - | - | 620 |
| 8.00 | 1.00 | - | 2.00 | - | - | - | - | 8.00 | - | 5.00 | - | - | - | - | - | -46 |

(a) Na₂CO₃ is the assumed product until either carbon or sodium is consumed. At that point either CO₂ or NaOH is formed. The carbonates of the heavy metals are unstable at the temperatures of interest.

(b) Hypothetical reaction, assumes CO₂ liberated.

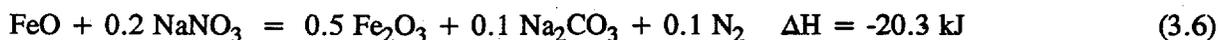
Table 3.3. (Contd)

| Reactants, Mols | | | Products, Mols ^(a) | | | | | | | | | |
|-------------------------|------------------|------|---------------------------------|-----------------|------------------|----------------|------------------|----|----|-------|-------------------|------|
| Fuel | H ₂ O | NaOH | Na ₂ CO ₃ | CO ₂ | H ₂ O | N ₂ | N ₂ O | NO | CO | NaOH | Na ₂ O | ΔH |
| NaCN | | | | | | | | | | | | |
| | | | 1 | - | - | 1 | - | - | - | - | - | -572 |
| NaNO₂ | | | | | | | | | | | | |
| | 1.667 | - | 1 | - | - | 1.33 | - | - | - | 0.667 | - | -645 |
| | 1.667 | - | 1 | - | - | 1.33 | - | - | - | - | 0.33 | -580 |
| NaCNO | | | | | | | | | | | | |
| | | | | | | | | | | | | |
| | 0.60 | - | - | 0.80 | 0.2 | - | 1.30 | - | - | - | - | -297 |
| | 0.6 | - | 0.40 | 1 | - | 0.20 | 1.30 | - | - | - | - | -323 |

(a) FeO and NiO are assumed as products except where indicated. If Fe₂O₃ is produced, then about 3 % more oxidant is required and produces about 3 % more energy.

the products will probably not occur; furthermore, several simultaneous reaction paths may be taken. Commonly, an efficiency of about 80% of the maximum theoretical enthalpy is found for explosive reactions (Dobratz and Crawford 1985).

It is notable that we usually observe NO being formed from slow, low-temperature reactions between ferrocyanides and nitrate-nitrite mixes (Scheele et al. 1992). It is not apparent in the laboratory-observed deflagration reactions, but may be difficult to observe under the test conditions. Some is undoubtedly formed. The reactions in Table 3.3 assume NiO and FeO are formed. Production of Fe₂O₃ would be equivalent to adding the reaction.



Several steps are involved in the ferrocyanide oxidation (Burger et al. 1991). The nature of these steps (i.e., the reaction mechanism) is not known. We have observed N₂O as a major gaseous product in our organic-reaction tests (Scheele et al. 1995). Kozlowski and Bartholomew (1968) observed N₂O in addition to N₂ when NaCHOO and NaC₂H₃O₂ were reacted with molten sodium nitrate or nitrite.

The formation of Na₂CO₃ is responsible for a significant contribution to the energy released at ordinary temperatures. At temperatures above about 1800 K, Na₂O is more stable and may form in place of the carbonate. The enthalpy values listed in Tables 3.2 and 3.3 illustrate the effect of NaOH and or H₂O on the reactions. The changes in enthalpy resulting from different sodium products can be computed from the following reactions; data are for 298 K:



These reactions are important at high temperatures. The reactions, their temperature dependence, and similar reactions for cesium are discussed in a later section.

The most significant heat-sink contributions to the enthalpy calculations at temperatures below about 700 K are from the solid-liquid and liquid-gas transitions. For water, this is vaporization, $\Delta H = 2263 \text{ J/g}$ (541 cal), which is by far the largest contribution in the system. As will be seen, water in nearly dry systems characteristic of Hanford wastes may more realistically be treated as hydrated salts with some contribution from a concentrated sodium hydroxide solution. The energy required to dry these materials is much greater than the heat of vaporization of water, as discussed below.

For NaNO_3 , the fusion enthalpy is 182 J/g (43.6 cal) at 580 K, and for NaNO_2 , 51.7 cal/g at 557 K. Detailed phase transitions are discussed below.

Variations in published heat capacity and transition data introduce an overall error of less than 3% up to about 800 K. Using a constant heat capacity instead of enthalpy tables (or heat-capacity equations) would produce a value about 15% to 20% low at 500 K. This error increases rapidly at higher temperatures and may be on the order of 40% at 700 K to 800 K (see Table A.3). Heat capacities are best compared per unit mass but there are still significant differences among the different compounds. Sodium hydroxide has a high heat capacity compared to, for example, NaAlO_2 . More importantly, it retains water to moderately high temperatures, further increasing its effective heat capacity.

Above about 800 K to 900 K, the decomposition of any excess nitrate or nitrite salts adds to the heat sink and may significantly limit the final reaction temperature. These decompositions are slow at 800 K to 1200 K, and the fraction decomposed must be estimated. Approximate values of the enthalpy at temperature T, relative to 60°C (333 K), $H_T - H_{333}$ are then calculated. Salt volatilization also begins as the upper temperature is approached. This topic is considered further in Section 4.0.

3.2 Thermal Data for Compounds

Water MW 18.01. Heating 1 g of water from 333 K to 373 K and vaporizing it requires 2443 J (584 cal). Using data from Table A.3, it is calculated that raising the temperature from 333 K (liquid) to 500 K (gas), for example, requires 2686 J. Water is by far the most important component in the waste tanks from the standpoint of prevention of high-temperature oxidation reactions.

The enthalpy for release of water from hydrates depends on the affinity of the compound. Many common salts show differences between the hydrate and the anhydrous salt of about 3100 to 4800 J/g of water, considerably greater than for the vaporization of pure water. Some hydrated compounds are stable to several hundred degrees, e.g., some of the silicates and aluminates.

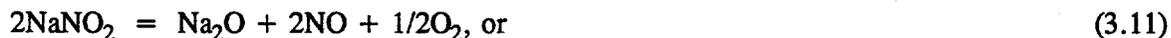
The hydroxides vary greatly in stability, hence the enthalpy for water loss varies. Forming $\text{FeO}(\text{OH})$ from $\text{Fe}(\text{OH})_3$ requires 22 kJ per mol (1222 J/g of water). Forming 1 g of water from the decomposition of NaOH requires 10.5 kJ, nearly 10 times more energy. The latter reaction is not expected. Rather, the important process is removal of water from a concentrated sodium hydroxide solution. This process, which is not complete until a temperature greater than 575 K is reached (Kirk-Othmer 1978), is discussed in Section 4.0.

Sodium nitrate MW 85.00. Barin (1989) indicates a solid-solid transition of 144.6 J/g at 548 K. No heat-capacity equation was found for the new solid. The error in using the lower temperature equation for the second solid phase from 548 K to 579 K is negligible, and calculated data agree with the enthalpy tables. Melting occurs at 579 K and requires 182.4 J/g.

Slow decomposition begins at about 875 K, and the pseudo-equilibrium between the nitrate, nitrite, and oxygen has been examined over many years (Oza 1945, Freeman 1956, Sirotkin 1959, Arvia et al. 1964, Bond and Jacobs 1966, Kust and Burke 1970). Many investigations of these reactions appear in the literature and include spectroscopic measurements of melts, gas analysis, and electrochemical measurements. An early but still very useful reference is the review by Stern (1972).

Nitrate salts decompose by several mechanisms. Heavy-metal salts often go directly to the metal oxide and NO_2 , or in some cases form both NO and NO_2 . In the case of alkali nitrates, which are of more interest to us, the picture is more confusing. It is generally accepted that the principal path for sodium and potassium nitrate is to form the corresponding nitrite and oxygen. This begins by 500°C and probably at measurable rates at lower temperatures. The next step is not as simple. Nitrites decompose to the oxide, e.g., Na_2O , NO , and O_2 , a process which may begin at as low as 320°C . A result of this step is the formation of NO_2 , which may in fact be produced directly. In turn, the nitrite can be reoxidized back to nitrate.

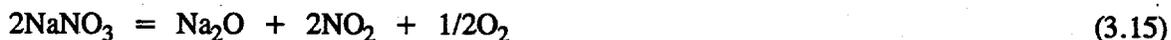
The important steps then appear to be:



Reaction (3.14) is reversible, as is (3.10) if the temperature is high enough, greater than about 600°C .

The mechanisms are still unclear; catalysts including metal oxides such as NiO , V_2O_3 , ZnO , may reduce the decomposition temperature and also seem to promote the formation of NO over N_2 . Na_2O_2 and perhaps other oxides are formed in the processes. No studies have indicated the formation of N_2O from the pure melts.

Reaction (3.10) requires 109 kJ/mol. The net decomposition reaction for NaNO_3 is



for which $\Delta H = 620 \text{ kJ}$ (3648 J/g NaNO_3).

Sodium Nitrite MW 68.00. Sodium nitrite melts at 557 K. The enthalpy change is 216.3 J/g. No solid transitions are reported. It begins to decompose at about 600 K to give Na_2O , NO , and NO_2 (Stern 1972). NO reoxidizes the nitrite to nitrate, producing N_2 . Thus, in the absence of oxygen the net reaction becomes



for which $\Delta H = 300 \text{ kJ}$ (2205 J/g NaNO_2).

The nitrate and nitrite decompositions are very endothermic. However, the reactions are slow at temperatures where they begin and may be incomplete even at considerably higher temperatures. Since the reactions are complex even in the pure salts, it is difficult to estimate the true heat capacity of the decomposing nitrate-nitrite system. The data of Bond and Jacobs (1966) show about 50% decomposition of both salts in 45 min at 925 K. Using activation energies from their data (169 kJ/mol for NaNO_3 , 179 kJ/mol for NaNO_2) suggests that the reaction may be about 50 times faster at 1125 K. Early thermal analysis experiments of Gordon and Campbell (1955) suggested complete decomposition at about 1075 K to 1100 K when a 5-g sample was heated at 15° per minute.

Complete and rapid decomposition of both salts to sodium oxide, oxides of nitrogen, oxygen, and some free nitrogen is expected above about 1300 K.

Ryan (Burger et al. 1973) observed some volatilization from the nitrate/nitrite system at 1075 K to 1125 K and a large loss at 1200 K to 1225 K. Volatilization as Na_2O would require about 117 kJ/mol (Glassner 1958). However, Na_2O has negligible volatility at 1200 K (Brewer and Margrave 1955). Possibly direct volatilization of the salts is occurring. Any source of water will produce NaOH , which is much more volatile than the nitrate.

Both the nitrate and nitrite salts are active oxidants and react vigorously with many reductants including organic compounds.

Sodium Aluminate MW 81.97. Heating to 475 K requires 143.5 J/g, to 525 K an additional 57.7 J/g, and from 525 K to 580 K requires 63.2 J/g. A single low-energy (15.9 J/g) solid-solid transition occurs at 740 K. Sodium aluminate is probably an actual component in many tanks, although it may always contain some NaOH . However, if it exists as a discrete compound, it is probably hydrated. Scanning thermal gravimetry (STG) of a laboratory sample showed three distinct water-loss steps. The first water loss of about 4% was complete at about 350 K, the second of about 6% at 430 K, and the third of a little over 10% was complete at about 510 K. Complete loss of the water of hydration would add about 730 J/g to the values listed in the appendix for NaAlO_2 .

Sodium Sulfate MW 142.04. Sodium sulfate is anhydrous at temperatures of concern. Solid-state transitions occur at 458 K (1.84 J/g) and 514 K (76.6 J/g). The melting point is 1157 K (167.8 J/g). Many waste tanks will contain this salt. The vapor pressure is about 0.15 torr at the melting point and is 1 torr at 1644 K. Above about 1370 K sodium sulfate begins to decompose if it is not pure; the products are SO_2 , SO_3 , O_2 , and Na_2O (Kirk-Othmer 1983). Sodium sulfate is one of the most stable metal sulfates.

Sodium Phosphate MW 163.94. The tertiary ortho-phosphate should exist at the pH values found in the waste tanks. It should be anhydrous at tank temperatures; no transitions are reported up to 900 K. However, it is not likely that Na_3PO_4 would precipitate as such. The phosphates of group two and the heavy metals are much more insoluble and the latter metals may be sufficiently abundant to remove most of the phosphate ions from solution. Laboratory preparations of sodium ortho-phosphate invariably contain NaOH (Whaley 1973), which makes the high-temperature behavior of sodium phosphate, including melting, questionable.

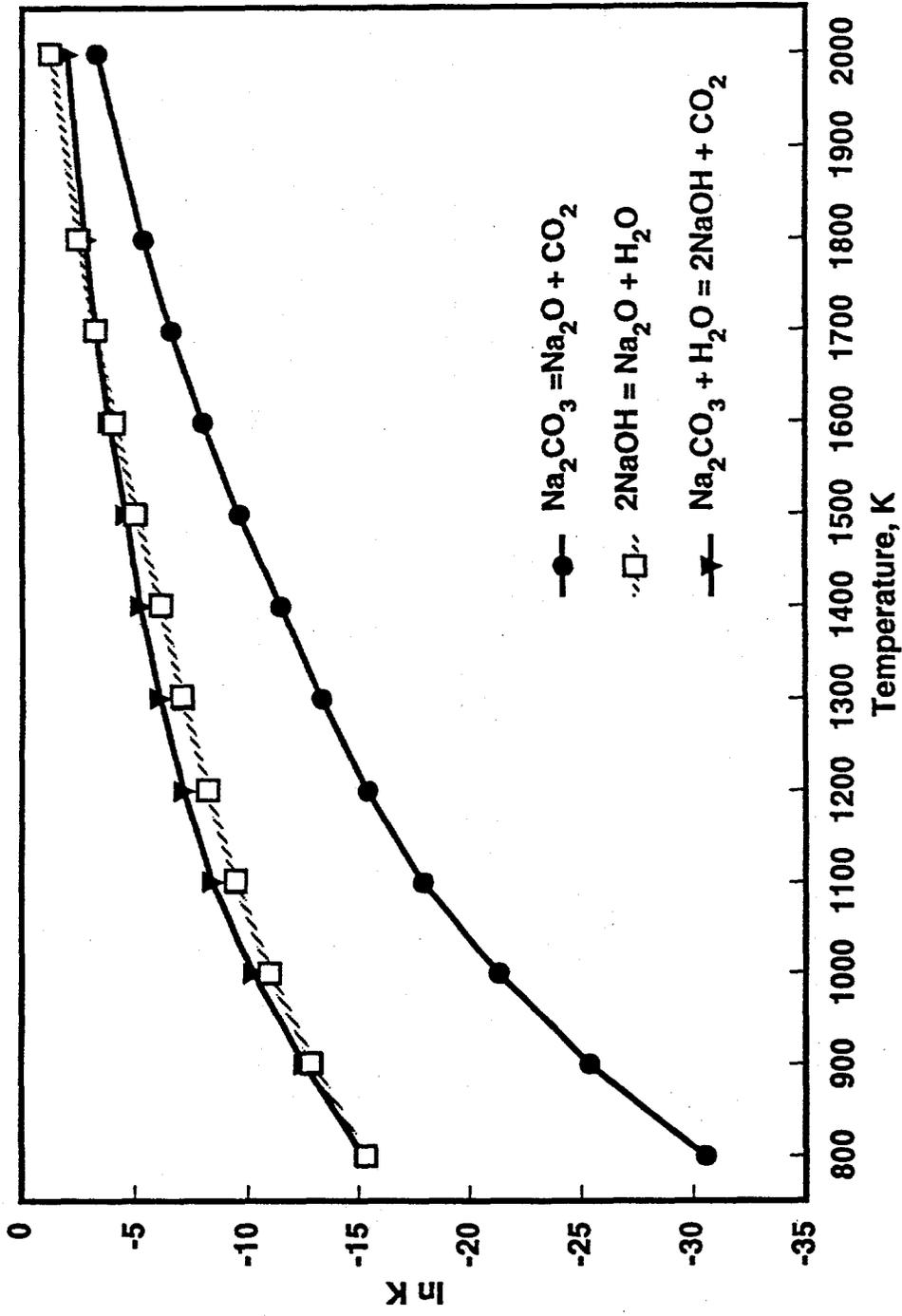
Iron and Nickel Oxides MW 71.85, 74.71. Nickel oxide undergoes two phase changes between below 600 K, but no energy change is reported. The first raises C_p ; the second lowers it to below the original value. The average is about 56 J/mol-deg, nearly equal to that of FeO. Since these oxides contribute only a small amount to the overall heat capacity, a constant value of 13 J/mol-deg or 0.75 J/g-deg could be used for the heat capacity with an error of about 3% over the calculation range. However, enthalpy data as a function of temperature are included in Table A.2.

The oxide, FeO, has no transitions in the range of interest. It is assumed to be the product for the ferrocyanide reactions. Other oxides (e.g., Fe_2O_3) may also form. The differences in heats of formation and heat capacities, on a mass basis, of the two oxides is negligible. The net heat of reaction is about 3% greater if ferric oxide rather than FeO is the product in ferrocyanide reactions.

Iron compounds will normally be present in waste tanks as a result of process chemical additions and from corrosion. Some form of ferric hydroxide may be a common form in the waste tank solids.

Ferric Hydroxide MW 106.87. $\text{Fe}(\text{OH})_3$ or perhaps in the form of a ferric oxide hydrate is very stable and very insoluble. Because of these properties and the generally oxidizing nature of the waste environment, the compounds may exist in appreciable amounts. No transitions are reported up to 1000 K for $\text{Fe}(\text{OH})_3$. However, dehydration is expected as the temperature is raised as discussed above. Fe(II) compounds are not expected to be in most of the tanks.

Sodium Carbonate MW 105.99, Sodium Oxide MW 61.98, Sodium Hydroxide MW 40.00. Sodium carbonate has one solid-solid transition at 723 K of 0.690 kJ/mol (6.7 J/g). The melting point is 1123 K and the enthalpy of fusion is 2339 J/g. The enthalpy of decomposition of the carbonate to CO_2 and Na_2O is 319.3 kJ/mol or 3008 J/g. Free-energy data showing conversion to the oxide or the hydroxide are illustrated in Figure 3.1. With CO_2 present, Na_2CO_3 is the stable species to about 1800 K to 2000 K. The equilibrium vapor pressure of CO_2 at 2000 K is calculated to be 20.6 torr. The decomposition requires 323 kJ/mol or 3046 J/g.



R9509035.1

Figure 3.1. Equilibrium Constants for Sodium Compound Reactions

Sodium hydroxide has a transition at 572 K with an enthalpy of 7.2 kJ (179.8 J/g) and melts at 596 K with an enthalpy of 6.6 kJ/mol or 164.8 J/g. It is the most soluble of the sodium compounds and might not exist in large amounts as a solid until the tank contents were quite dry. On the other hand, the carbonate will probably be the first to precipitate. At high temperatures, water aids in the conversion of the carbonate to the hydroxide, as seen from Figure 3.1. The calculated $\text{CO}_2/\text{H}_2\text{O}$ ratio is 0.2 at 1700 K and 1.0 at 2300 K. These calculations are only approximate since they assume pure phases of the solid and liquid compounds are involved. Equilibria among the similar cesium compounds are discussed in the Volatility Section.

Sodium oxide, Na_2O , has two solid-solid transitions, at 1023 K with 1.8 kJ/mo (28.9 J/g) and at 1423 K with 11.9 kJ/mol (182.0 J/g). It melts at 1405 K with an enthalpy of 47.7 kJ/mol or 769 J/g. It would not normally exist in the tanks and is considered only as a hypothetical reaction product and as a high-temperature decomposition product of some sodium salts.

Sodium hydroxide is the stable high-temperature species if water vapor is present. This is discussed further under High-Temperature Reactions, Section 4.3. In addition, it may have special importance as a heat sink. As the contents of most tanks approach dryness, a NaOH solution saturated at a temperature well above the normal boiling point of water may be the last aqueous phase. The phase diagram for NaOH-water shows several compounds and the system is not anhydrous until 614 K is reached (Kirk-Othmer 1978). The heat capacity may be approximated by combining the heat of solution of NaOH with H_T-H_{333} data for water and NaOH. Above about 1400 K, the vapor pressure of molten NaOH is significant. At 1500 K the vapor pressure of NaOH gas is calculated from free-energy data to be 0.08 atm and for $\text{Na}_2(\text{OH})_2$ 0.03 atm. At the normal boiling point, 1827 K, the gas is the monomer. For 1 g of a 60% NaOH solution (approximately the concentration of a saturated solution at 60°C), effective H_T-H_{333} values are calculated and are included in Table 4.5 and shown graphically in Figure 4.5. The heat of vaporization is included at high temperature.

Sodium Nickel Ferrocyanide MW 316.60. No heat-capacity data were found for this or similar compounds. KCN and $\text{K}_3\text{Co}(\text{CN})_6$ have identical heat capacities per gram. On this basis, the heat capacity of $\text{Na}_2\text{NiFe}(\text{CN})_6$, (FeCN) , and thus its enthalpy, could be approximated from that for NaCN , 1.42 J/g-K. It is not used in calculations in this paper.

Bismuth Phosphate MW 303.95. No transitions are reported up to 900 K. No other thermodynamic data were found. The BiPO_4 may be hydrolyzed to species such as $\text{BiO}(\text{OH})$ in the waste tanks.

Sodium Aluminum Silicate, $\text{Na}_2\text{AlSiO}_2$, Nepheline MW 142.05. Transitions at 467 K and 1180 K are reported, both with zero enthalpy change. Nepheline and analcite are not necessarily present in the waste tanks but are taken as representative of Na-Al-Si compounds which could be formed.

Sodium Aluminosilicate, $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, Analcite MW 220.15. No transitions are listed for analcite. Based on free-energy data for the hydrated and anhydrous forms (Barin 1989), dehydration will take place slowly, starting at about 475 K. The enthalpy associated with the water loss is calculated to be 74 kJ/mol (335 J/g), or about 4100 J/g water. We have found from differential scanning calorimetry (DSC) and scanning thermogravimetry (STG) measurements that many hydrates in complex mixtures lose water slowly, often requiring temperatures of 500 K or above. The heat capacity of analcite itself is about 0.2 J/g-K greater than the heat capacity for the anhydrous compound.

Hydrated analcite may be typical of several compositions that exist in the waste tanks that will retain water to 450 K to 550 K. Thus, about 10% by weight is not an unreasonable water content for dried waste. Another example is sodium aluminate, discussed above, which, in laboratory experiments, lost 17% water by 513 K. About 200 to 600 J/g, depending on the temperature, would be added to $H_T - H_{333}$ values listed in the Appendix A, if the compounds are hydrated with one molecule of water.

Nickel and Cobalt Sulfides MW = 90.77, 91.00. NiS undergoes an endothermic transition of 6.4 kJ/mol (70.3 J/g) at 652 K. Sulfides of both metals will be oxidized before these temperatures are reached. Concentrations are too low to contribute significantly to the heat capacity, but both compounds react exothermally with nitrates or nitrites.

Organic Compounds. A large number of representative compounds are listed in Tables 4.1 and 4.2. Most are not discussed individually but some generalizations can be made. All acids should exist in anion form (as sodium salts if solids). Ethylenediaminetetraacetic acid (EDTA) and hydroxyethyl ethylenediaminetriacetic acid (HEDTA) can be considered to be typical of all amine-based complexants. These were used in large amounts. Klem (1988) has compiled a list of chemicals used in Hanford processes; many of the organic compounds listed will have entered the waste tanks. Possible mechanisms for concentration of organic wastes have been surveyed by Gerber (1992).

Hexone (methyl isobutyl ketone) and tributyl phosphate (TBP) were the process solvents used in largest quantity. Little hexone should remain, due to its volatility and reactivity. Iso-butyric acid is a moderately stable decomposition product. If TBP remained in contact with an aqueous phase for several years, then it should be hydrolyzed to dibutyl phosphate (DBP), which would exist as the sodium salt, and butyl alcohol, which would slowly oxidize. In a basic system the hydrolysis of the phosphate ester becomes very slow at this point (Burger 1955). However, radiation will continue the destruction and may have converted much of it to hydrocarbons and carboxylic acids. The phosphate ion is an ultimate product. Dibutyl butyl phosphonate (DBBP) is slightly more stable and slightly more soluble in water than is TBP. Otherwise it and other phosphate solvents used can be considered to be similar to TBP.

A variety of hydrocarbons have been added to the tanks, and radiolysis may have rearranged many of the molecules. The largest source is likely diluent from TBP-extraction processes. The original diluent was a kerosene or spray-base type; in later years it was replaced by predominately n-paraffinic hydrocarbons (n-dodecane). In this paper, calculations were made for both decane and dodecane. Complexing agents including EDTA, HEDTA, and glycolic acid were used in large quantities at one time for one separations process. Another source of organic compounds is decontamination agents

used in the plant. These include a variety of detergents, solvents, and complexing agents. A few smaller molecules, most of which are aqueous soluble, are included in the tables as being representative of possible decomposition products. Vinyl pyridine is included as a model for a class of ion-exchange resins.

Highly sensitive compounds such as nitrate esters, peroxides, nitramines, fulminates, perchlorates, compounds with triple bonds, etc., are not expected to exist in the waste tanks (Martin 1985) and are not considered here. Hobbs (1992) made an extensive study of similar Savannah River waste tanks and reached similar conclusions.

Gaseous Products. Data from the enthalpy tables (Tables A.1 and A.2) can be used directly. Thermal data for water are for the gaseous state. Homogeneous gas reactions are not included in this study.

4.0 Discussion

The actual temperatures reached and the general behavior of the reactive mixtures depend on a variety of factors, as discussed below.

4.1 Thermal Data for Reactions

The calculated enthalpies of reaction at 333 K (reactants and products at 60°C) are within about 1% to 2% of the values at 298 K. Thus, the data from Table A.1 (Appendix) can be used to calculate tank reactions at 333 K. Table 4.1 summarizes data for stoichiometric reactions with sodium nitrate, assuming complete oxidation and the formation of N₂. Table 4.2 lists similar data for sodium nitrite. Data are given for the maximum energy reaction and are presented per mol of fuel, per gram, per gram of carbon, and also in terms of an energy *density* or heat of reaction per gram of stoichiometric mix.

Note that there are significant differences in the energy per gram of reactant and in the amount of oxidant required per gram. Hydrocarbons are high in energy, which shows up in TBP and DBP. Partial oxidation lowers the energy available, of course. An example is the trend from acetate to hydroxyacetate, to dihydroxyacetate, and finally to oxalate. Further oxidation, to CO₂ and H₂O, produces only a small energy. Ferrocyanides rate high in energy.

Note that values listed for the energy per gram of reactant vary over a factor of about 25, or if sodium oxalate is not considered, over a factor of about 14. The energy per gram of reactant-oxidant mix is also interesting since the relative weight of oxidant required per gram of reactant varies over a range from 1 to about 15. The energy per gram of reactant has obvious importance. But the energy per gram of mix may also be significant since the composition range covered may be that found in typical settled tank sludges or other tank waste forms. Also, as will be seen, excess nitrate is an excellent heat sink, becoming much more effective as the temperature rises. There are several reasons: (1) the specific heat of the solid is greater than for most solids; (2) solid-solid transition and the heat of melting add a large amount to the enthalpy; and (3) at slightly higher temperatures the enthalpy of decomposition is added. Thus, different *fuels* in the same mass concentration range can represent quite different hazards. Sodium nitrite behaves similarly to the nitrate salt.

It was noted that carbon content is a poor measure of reaction energy. Figure 4.1 illustrates one attempt at finding a composition basis better than carbon content for comparing heats of reaction. None of the correlations are very good. Plotting the same variables against energy per gram of mix gave similar results. The compounds used are indicated in Table 4.1.

The computed reaction energies are for the maximum energy path. It was noted that a lower energy path is possible. Also for many organic materials, it is possible that a thermal decomposition followed by volatilization of fragments before oxidation can occur. Also, with moderately volatile compounds like dodecane, partial or complete volatilization is possible, depending on the heating regime and the confinement. Thus the energies shown in Tables 4.1 and 4.2 are seldom realized.

Table 4.1. Reaction Energy at 298 K, Sodium Nitrate Oxidant

| Cpd | MW | %C | -ΔH _f | -ΔH _{rxn} /mol | -ΔH _{rxn} /g | -ΔH _{rxn} /gC | mols oxid | -ΔH _{rxn} /g mix | mols gas |
|--|-------|------|--------------------|-------------------------|-----------------------|------------------------|-----------|---------------------------|----------|
| C* | 12 | 100 | 0.0 | 314.5 | 26.2 | 26.2 | 0.8 | 3.93 | 1.4 |
| CH ₄ * | 16.04 | 74.9 | 74.8 | 639.7 | 40.0 | 53.3 | 1.6 | 4.14 | 3.0 |
| C ₁₀ H ₂₂ * | 142.3 | 84.4 | 301.0 | 5063 | 35.6 | 42.2 | 12.4 | 4.23 | 4.0 |
| C ₁₂ H ₂₆ * | 170.3 | 84.6 | 350.9 | 6046 | 35.5 | 42.0 | 14.8 | 4.23 | 25.0 |
| Dodecane | | | | | | | | | |
| CH ₃ OH | 32.0 | 37.5 | 238.7 | 521.1 | 16.3 | 43.4 | 1.2 | 3.87 | 3.0 |
| Methanol | | | | | | | | | |
| C ₄ H ₉ OH* | 74.1 | 64.8 | 327.4 | 1973 | 26.7 | 41.2 | 4.8 | 4.09 | 9.0 |
| n-Butanol | | | | | | | | | |
| HCOOH | 46.0 | 26.1 | 424.7 | 170.9 | 3.71 | 14.2 | 0.4 | 2.13 | 1.0 |
| Formic acid | | | | | | | | | |
| NaCHOO* | 68.1 | 17.6 | 666.5 | 176.8 | 2.60 | 14.2 | 0.4 | 1.73 | 1.0 |
| C ₁₂ H ₂₂ O ₁₁ | 342.3 | 42.1 | 2225 | 4204 | 12.3 | 29.2 | 9.6 | 3.63 | 23.0 |
| Sucrose | | | | | | | | | |
| C ₇ H ₇ N* | 105.1 | 80.0 | 155.6 | 2751 | 26.2 | 32.7 | 7.0 | 3.92 | 11.0 |
| Vinyl Pyridine | | | | | | | | | |
| CH ₃ COOH | 60.0 | 20.0 | 484.5 | 627.6 | 10.45 | 26.1 | 1.60 | 3.20 | 4.0 |
| Acetic acid | | | | | | | | | |
| NaCH ₃ COO* | 82 | 29.3 | 708.8 | 650.7 | 7.94 | 27.1 | 1.60 | 2.98 | 3.0 |
| NaCH ₂ OHCOO* | 98 | 24.5 | 900.8 | 498.4 | 5.08 | 20.7 | 1.2 | 2.49 | 3.0 |
| Sodium glycolate | | | | | | | | | |
| NaCH(OH) ₂ COO | 114 | 21.0 | 1070 | 369 | 3.24 | 15.4 | 0.8 | 2.03 | 3.0 |
| Sodium glyoxylate | | | | | | | | | |
| NaC ₃ H ₇ COO* | 110.1 | 43.6 | 774 ^(a) | 1618 | 14.7 | 33.7 | 4.0 | 3.60 | 7.0 |
| Sodium butyrate | | | | | | | | | |
| Na ₂ C ₂ H ₄ (COO) ₂ * | 162.1 | 29.6 | 1420 | 1097 | 6.77 | 22.8 | 2.8 | 2.74 | 5.0 |
| Sodium succinate | | | | | | | | | |
| Na ₂ (CHOH) ₂ (COO) ₂ * | 194.1 | 24.7 | 1771 | 825 | 4.25 | 17.2 | 2.0 | 2.27 | 5.0 |
| Sodium tartrate | | | | | | | | | |
| Na ₂ C ₂ O ₄ * | 134.0 | 17.9 | 1318.0 | 166.4 | 1.24 | 6.95 | 0.4 | 1.01 | 1.2 |
| Sodium oxalate | | | | | | | | | |
| C ₆ H ₈ O ₇ | 192.1 | 37.5 | 1543.9 | 1427 | 7.43 | 19.8 | 3.6 | 2.86 | 10.0 |
| Citric acid | | | | | | | | | |

Table 4.1. (contd)

| Cpd | MW | %C | $-\Delta H_f$ | $-\Delta H_{rx}/\text{mol}$ | $-\Delta H_{rx}/\text{g}$ | $-\Delta H_{rx}/\text{gC}$ | mols oxid | $-\Delta H_{rx}/\text{g mix}$ | mols gas |
|---|----------------|--------------|--|-----------------------------|---------------------------|----------------------------|------------|-------------------------------|--------------|
| $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7^*$ Sodium citrate | 258.1 | 27.9 | 2260 ^(e) | 1460 | 5.66 | 20.3 | 3.6 | 2.59 | 7.0 |
| $\text{NaCH}_2\text{NH}_2\text{COO}^*$ Sodium glycinate | 97.0 | 24.75 | 765 ^(e) | 693 | 7.14 | 28.9 | 1.8 | 2.79 | 4.0 |
| $\text{NaCONH}_2\text{COO}^*$ Sodium oxamate | 111 | 25.3 | 911.1 ^(e) | 387.1 | 3.49 | 16.1 | 1.0 | 1.98 | 3.0 |
| EDTA Ethylenediamine tetraacetic acid | 292.2 | 41.1 | 1759 | 3317 | 11.4 | 27.6 | 8.0 | 3.41 | 18.0 |
| Na_4EDTA^* HEDTA ^(e) Hydroxyethyl ethylenediamine triacetic acid | 380.2 275.2 | 31.6 43.6 | 2715 ^(e) 1552 ^(e) | 3348 3686 | 8.81 13.4 | 27.9 30.7 | 8.0 8.8 | 3.16 3.60 | 15.0 20.0 |
| N_3HEDTA^* $(\text{CH}_3)_2\text{NH}$ Dimethyl amine | 344.2 45.1 | 34.9 53.3 | 2247 ^(e) 43.9 | 3708 1292 | 10.8 28.6 | 30.9 54.0 | 8.8 3.0 | 3.39 4.31 | 17.0 7.5 |
| $(\text{CH}_3)_2\text{NNO}$ Diethyl nitrosoamine | 74.1 | 32.4 | -4.6 | 1273 | 17.2 | 53.1 | 2.4 | 4.56 | 6.0 |
| NaCN | 49.0 | 24.4 | 90.7 | 565.3 | 11.5 | 47.1 | 1.0 | 4.22 | 1.0 |
| $\text{Na}_2\text{NiFe}(\text{CN})_6^*$ Sodium nickel ferrocyanide | 316.6 | 22.7 | 0 ^(e) | 3012 | 9.50 | 27.1 | 6.0 | 3.64 | 8.0 |
| TBP [*] Tributyl phosphate | 266.3 | 54.1 | 1450 | 5920 | 22.2 | 41.1 | 14.4 | 3.97 | 27.0 |
| NaDBP [*] Sodium dibutyl phosphate | 232.2 | 41.4 | 1500 ^(e) | 4050 | 17.4 | 42.1 | 9.6 | 3.85 | 18.0 |
| $\text{Na}_6\text{H}_6\text{HexPO}_4^*$ Sodium di2-ethylhexyl phosphate | 344.4 | 55.7 | 1750 ^(e) | 7920 | 23.0 | 41.3 | 19.2 | 4.01 | 34.0 |
| NiS | 90.8 | - | 82.0 | 291 | 3.18 | - | 1.6 | 2.74 | 0.8 |
| $\text{C}_{11}\text{H}_{23}\text{COOH}$ Dodecanoic acid | 200.3 | 72.0 | 774.6 | 5514 | 27.5 | 38.2 | 13.6 | 4.07 | 24.0 |
| $\text{C}_{11}\text{H}_{25}\text{COONa}$ | 222.3 | 64.2 | 1015 ^(e) | 5507 | 24.8 | 38.6 | 13.6 | 4.00 | 23.0 |

Table 4.1. (contd)

| Cpd | MW | %C | - ΔH_f | - $\Delta H_{rx}/mol$ | - $\Delta H_{rx}/g$ | - $\Delta H_{rx}/gC$ | mols oxid | - $\Delta H_{rx}/g$ mix | mols gas |
|----------------------------------|-------|------|----------------|-----------------------|---------------------|----------------------|-----------|-------------------------|----------|
| TNT | 227.1 | 37.0 | 66.9 | 2875 | 12.7 | 34.2 | 4.2 | 4.92 | 11 |
| Trinitrotoluene | | | | | | | | | |
| PETN | 316.2 | 19.0 | 538.5 | 2317 | 7.35 | 38.6 | 0.8 | 6.03 | 11 |
| Pentaerythritol tetra nitrate | | | | | | | | | |
| TNT (detonation) | | 37.0 | 66.9 | 1226 | 5.4 | 14.6 | 0.0 | 5.70 | - |
| PETN (detonation) | | 19.0 | 538.5 | 2287 | 6.32 | 33.2 | 0.0 | 7.24 | - |

* Compounds used in Figure 4.1.

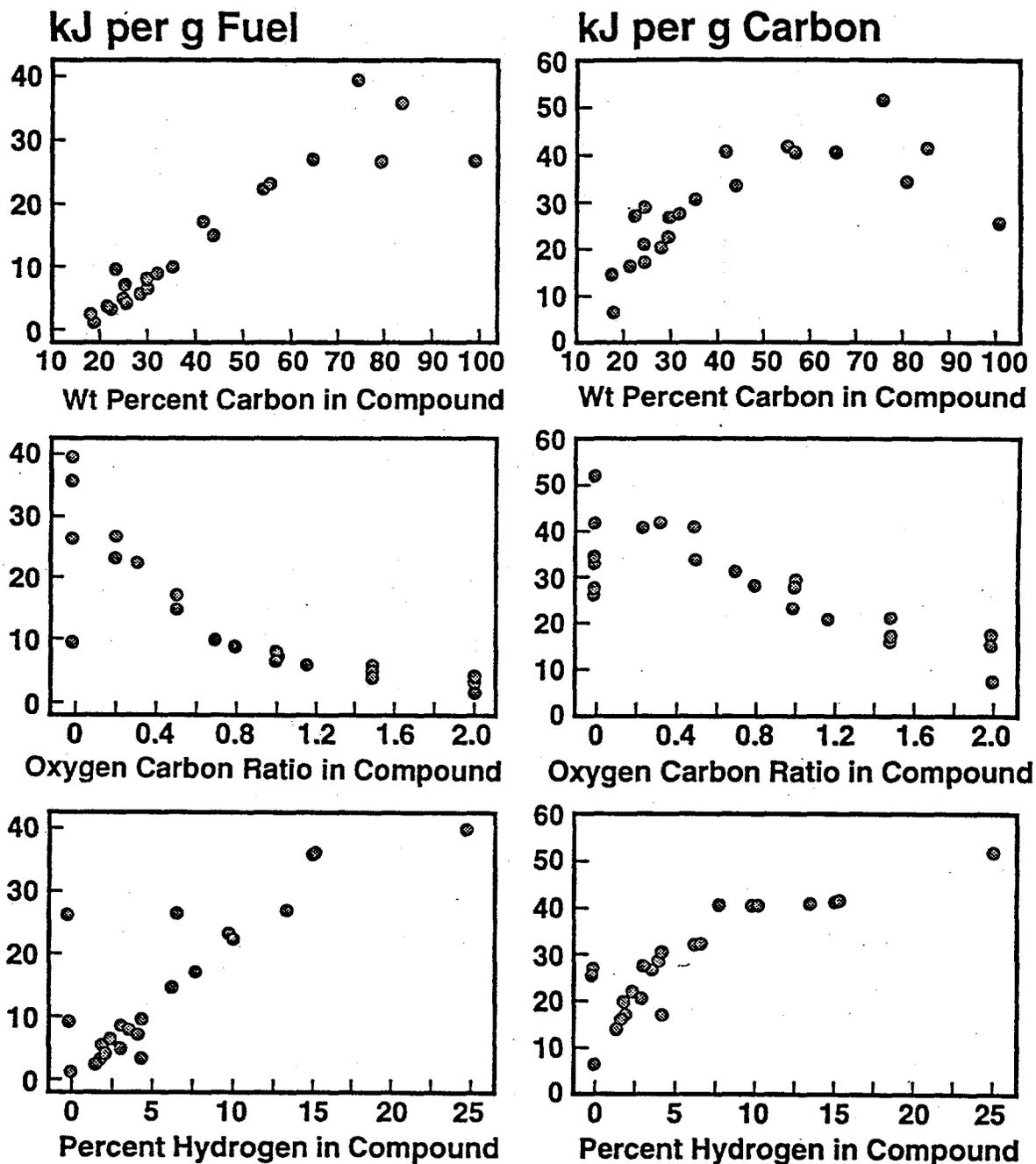
(a) ΔH_f estimated as described in text. ΔH_{rx} will be uncertain to ± 10 kJ per Na atom.

Table 4.2. Reaction Energy at 298 K, Sodium Nitrite as Oxidant

| Cpd (b) | MW | %C | ΔH_f | $-\Delta H_{rx}/\text{mol}$ | $-\Delta H/g$ | $-\Delta H/gC$ | mols oxid | $-\Delta H/g \text{ mix}$ | mols gas |
|--|-------|------|---------------------|-----------------------------|---------------|----------------|-----------|---------------------------|----------|
| NaCH ₃ COO | 92 | 29.3 | 708.8 | 836 | 10.2 | 34.8 | 2.67 | 3.14 | 3.0 |
| NaCHOO | 68 | 17.6 | 666.5 | 224 | 3.29 | 18.7 | 0.667 | 1.96 | 1.0 |
| C ₄ H ₉ OH | 74.1 | 64.8 | 327.4 | 2536 | 34.2 | 52.8 | 8.0 | 4.05 | 4.5 |
| CH ₄ | 16 | 74.9 | 74.8 | 786 | 49.2 | 65.7 | 2.667 | 3.93 | 3.0 |
| CH ₂ OHCOONa | 98 | 24.5 | 900.8 | 638 | 6.91 | 26.6 | 2.0 | 2.70 | 3.0 |
| CH ₂ NH ₂ COONa | 97 | 24.7 | 765 | 901 | 9.20 | 37.2 | 3.0 | 2.95 | 6.0 |
| C ₁₀ H ₂₂ | 142.3 | 84.4 | 301 | 6455 | 45.4 | 53.8 | 20.67 | 4.12 | 21.0 |
| C ₁₂ H ₂₆ | 170.3 | 84.6 | 350.9 | 7714 | 45.4 | 53.7 | 24.67 | 4.12 | 25 |
| C | 12 | 100 | 0.0 | 407 | 33.9 | 33.9 | 1.33 | 3.91 | 1 |
| NaDBP | 232.2 | 41.4 | 1500 ^(e) | 5160 | 22.2 | 53.6 | 16.0 | 3.86 | 18.0 |
| Nadi(2-ethylhexyl)PO ₄ | 344.4 | 55.7 | 1750 | 10165 | 29.4 | 52.8 | 32.0 | 3.96 | 34 |
| TBP | 266.3 | 54.1 | 1450 | 7588 | 28.5 | 52.7 | 24.0 | 3.95 | 28 |
| C ₇ H ₇ N | 105.1 | 80.0 | 155.6 | 3562 | 33.9 | 42.4 | 11.67 | 3.91 | 11 |
| CH(OH) ₂ COONa | 114 | 21.0 | 1070 | 449 | 3.95 | 18.8 | 1.33 | 2.18 | 3.0 |
| CONH ₂ COONa | 111 | 25.3 | 911 ^(e) | 503 | 4.53 | 17.9 | 1.67 | 2.23 | 3.0 |
| Na ₂ C ₂ O ₄ | 134 | 17.9 | 1318 | 213 | 1.59 | 8.88 | 0.67 | 1.18 | 1.0 |
| Na ₃ C ₆ H ₅ O ₇ | 258 | 27.9 | 2260 ^(e) | 1877 | 7.28 | 26.1 | 6.0 | 2.79 | 8.0 |
| Na ₂ C ₂ H ₄ (COO) ₂ | 162.1 | 29.6 | 1420 | 1421 | 8.77 | 29.6 | 4.67 | 2.94 | 6.0 |
| Na ₂ (CHOH) ₂ (COO) ₂ | 194.1 | 24.7 | 1771 | 1057 | 5.44 | 22.0 | 3.33 | 2.48 | 6.0 |
| Na ₄ EDTA | 380.2 | 31.6 | 2715 | 4274 | 11.24 | 36.7 | 13.33 | 3.28 | 15.5 |
| Na ₃ HEDTA | 344.2 | 34.9 | 2274 | 4727 | 13.7 | 40.1 | 14.67 | 3.48 | 16.0 |
| Na ₂ N ₁ Fe(CN) ₆ | 316.6 | 22.7 | 0 | 3710 | 11.7 | 51.5 | 10.0 | 3.68 | 8.0 |
| NiS | 90.8 | - | 82.0 | 726 | 7.98 | - | 2.67 | 2.64 | 1.33 |
| NaCN | 49 | 24.4 | 90.7 | 583.6 | 11.9 | 28.8 | 1.67 | 4.95 | 1.33 |
| NaC ₃ H ₇ COO | 110.1 | 43.6 | 774 | 2081 | 18.9 | 43.3 | 6.67 | 3.65 | 7.0 |
| C ₆ H ₆ O ₇ | 192.1 | 37.5 | 1543.9 | 1844 | 9.60 | 25.6 | 6.0 | 2.55 | 13.0 |
| C ₁₁ H ₂₃ COONa | 222.3 | 64.2 | 1015 ^(e) | 7083 | 31.9 | 49.6 | 22.67 | 3.96 | 23 |

(e) ΔH_f estimated as described in text. ΔH_{rx} will be uncertain to $\pm 10 \text{ kJ}$ per Na atom.

(b) See Table 4.1 for names of compounds



S9406007.15B

Figure 4.1. Energy Available from Nitrate Reactions as a Function of Hydrogen, Carbon, and Oxygen Content of the Fuel. Compounds used are identified in Table 4.1.

Included in the tables is the volume of gas produced. This quantity, to which can be added steam from excess water volatilization, may be important because of pressure that could develop in a tank.

4.2 Effect of Diluents and Temperature Change

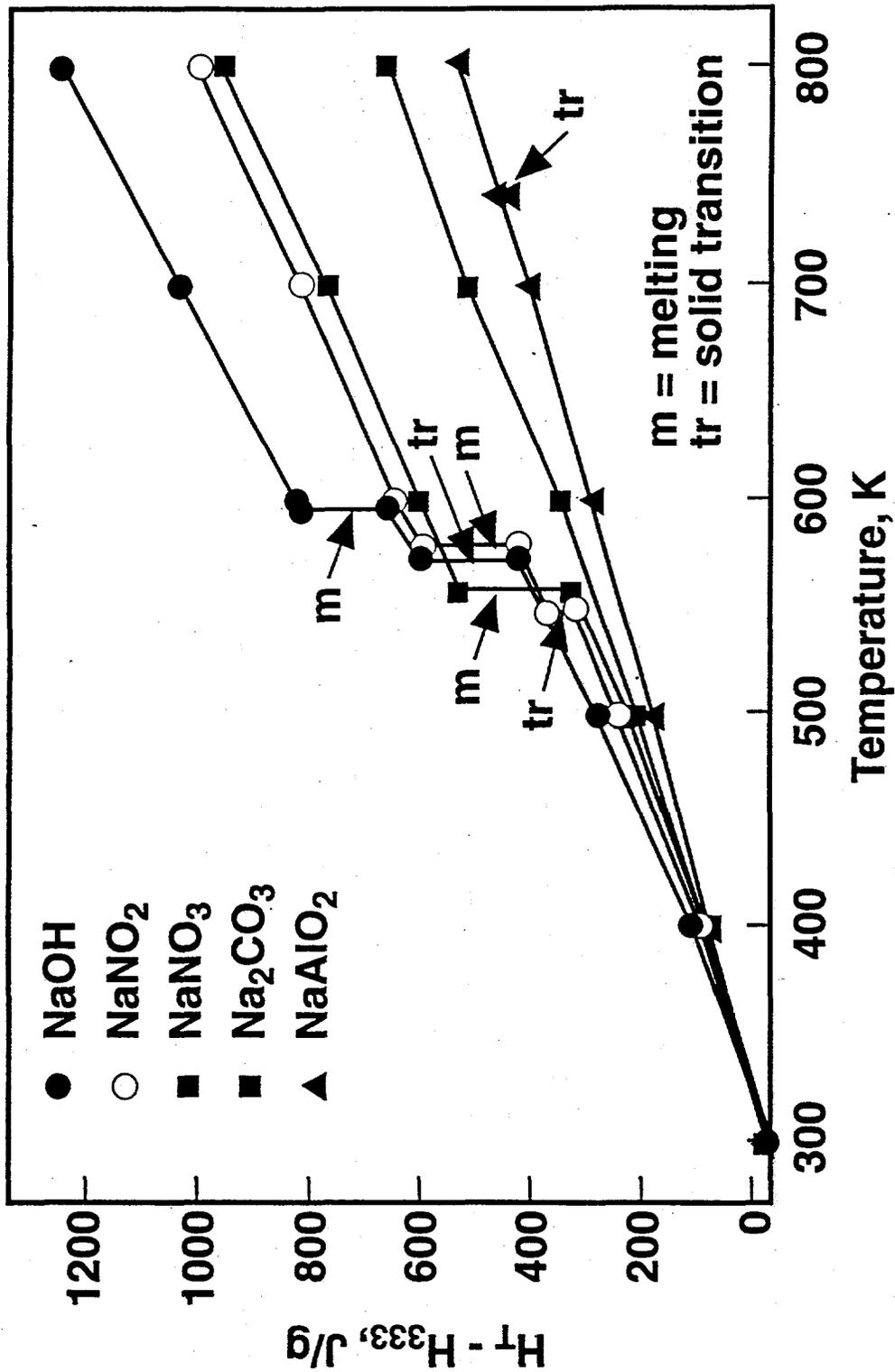
Using the 333 K reference point, roughly the temperature of a typical waste tank, the energy available at a given reaction temperature, ΔH_T^A , (not the enthalpy of reaction at that temperature) can be calculated for each reaction of interest.

$$\Delta H_T^A = \Delta H_{333} - \sum_i m_i (H_T - H_{333})_i \quad (4.1)$$

Here m_i is the mass of the i th component of the reaction products; $(H_T - H_{333})_i$, its enthalpy (integrated heat capacity at T relative to 333 K); and ΔH_{333} , the enthalpy of reaction at 333 K. These values can then be equated to the enthalpies of various tank constituents to compute the adiabatic temperature rise for a given reactant mixture. This is the temperature at which ΔH_T^A is equal to $\sum_j m_j (H_T - H_{333})_j$ for the excess oxidants and diluents in the mix. A comparison of the enthalpies of several different diluents is shown in Figure 4.2. The figure shows the solid-state transitions and the melting transitions of the pure compounds. Note that nitrate and nitrite salts will behave as diluents if in excess of the concentration is required for oxidation.

Table 4.3 lists the calculated available energy from the reactions of several fuels with sodium nitrate at different temperatures up to 1000 K. Figure 4.3 presents nitrate reaction data to 2000 K for three potential fuels. Included are curves showing the enthalpy of several combinations of sodium nitrate, water, sodium carbonate, and analcite. The point at which an available energy curve crosses the enthalpy curve of the mixture is the theoretical maximum temperature that would be reached. Figure 4.4 shows data for several other organic compounds. The maximum theoretical adiabatic temperature for a stoichiometric mixture of oxidant and fuel is obtained by extending the available energy curve to the enthalpy = 0 line. Real values will always be somewhat less, as discussed in Section 4.6.

Table 4.4 shows the energy required to heat an arbitrary mix of compounds from 333 K to higher temperatures, assuming no decomposition. It is apparent that all of the reactant mixes of Table 4.3, consisting of 1 g of fuel and a stoichiometric mass of oxidant, except for $\text{Na}_2\text{C}_2\text{O}_4$, would heat this mixture to greater than 1000 K. This mix contains only the water corresponding to the tetrahydrate of FeCN, about 3%. If the amount of water were 0.6 g, about 10% by weight, the corresponding energy requirements at each temperature would be 1850, 2325, 3300, 3990, 4670, 5340, and 6030 J. In this case, the reaction temperature for NaEDTA would reach 1000 K, but with NaCH_3COO it would not.



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Figure 4.2. Enthalpies, Including Transitions of Significant Inorganic Compounds

Table 4.3. Energy Available at Different Temperatures

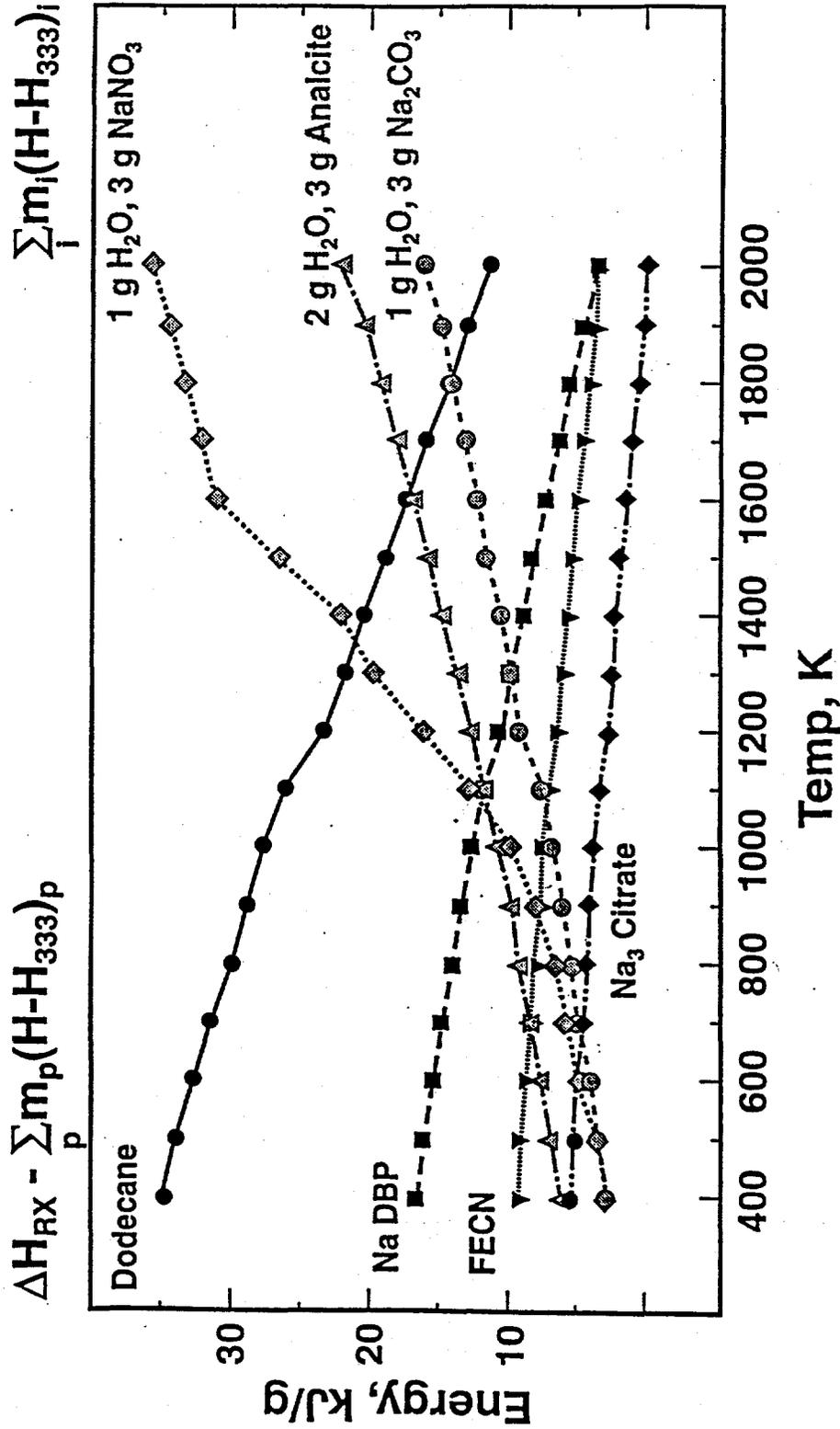
| Compound (fuel) | J/g of Fuel | | | | | | |
|---|-------------|--------|--------|--------|--------|--------|--------|
| | 400 K | 500 K | 600 K | 700 K | 800 K | 900 K | 1000 K |
| NaEDTA ^(a) | 8,545 | 8,210 | 7,791 | 7,373 | 6,960 | 6,540 | 6,309 |
| Na ₂ NiFe(CN) ₆ | 9,330 | 9,046 | 8,736 | 8,385 | 8,046 | 7,715 | 7,368 |
| NaCH ₃ COO | 7,719 | 7,381 | 7,008 | 6,590 | 6,192 | 5,774 | 5,356 |
| NaDBP | 17,070 | 16,500 | 15,600 | 15,225 | 14,560 | 13,855 | 13,137 |
| Na ₂ C ₂ O ₄ | 1,100 | 950 | 782 | 594 | 410 | 234 | 42 |

When examining nitrate or nitrite concentrations it is important to consider the stoichiometry. Consider a composition of 5 g NaNO₃, 2 g NaAlO₂, 1.0 g H₂O, and 1 g NaOH. Using data from Table A.3, it would require 7.32 kJ to heat this mixture to 700 K, 8.67 kJ to 800 K, 10.2 kJ to 900 K, and 11.6 kJ to 1000 K. If this mixture is combined with 1 gram of fuel (10% by weight), with 1 g of FeCN there is 3.39 excess nitrate; with 1 g of NaDBP, 1.93 g; and with Nadodecanoate, only 0.35 g. The FeCN mixture would reach a temperature of about 750 K while the NaDBP mixture would exceed 1000 K. Thus, depending on the type of fuel present, a large amount of nitrate or nitrite salt can either be a hazard or a safety cushion. What may be an excess of oxidant for one fuel could be sub-stoichiometric for another. Of course, a reaction will still occur with a large excess of oxidant; but it may be less energetic and slower.

Again, it is emphasized that these calculations give the maximum temperature that could be reached. They assume a single reaction path by the maximum energy route, no decomposition of salts except for dehydration of analcite, and that all water behaves as liquid H₂O. As will be seen, other decomposition reactions become significant heat sinks at temperatures in this range. They also assume that the system is truly adiabatic which in real cases is only approached by large masses or very fast reactions.

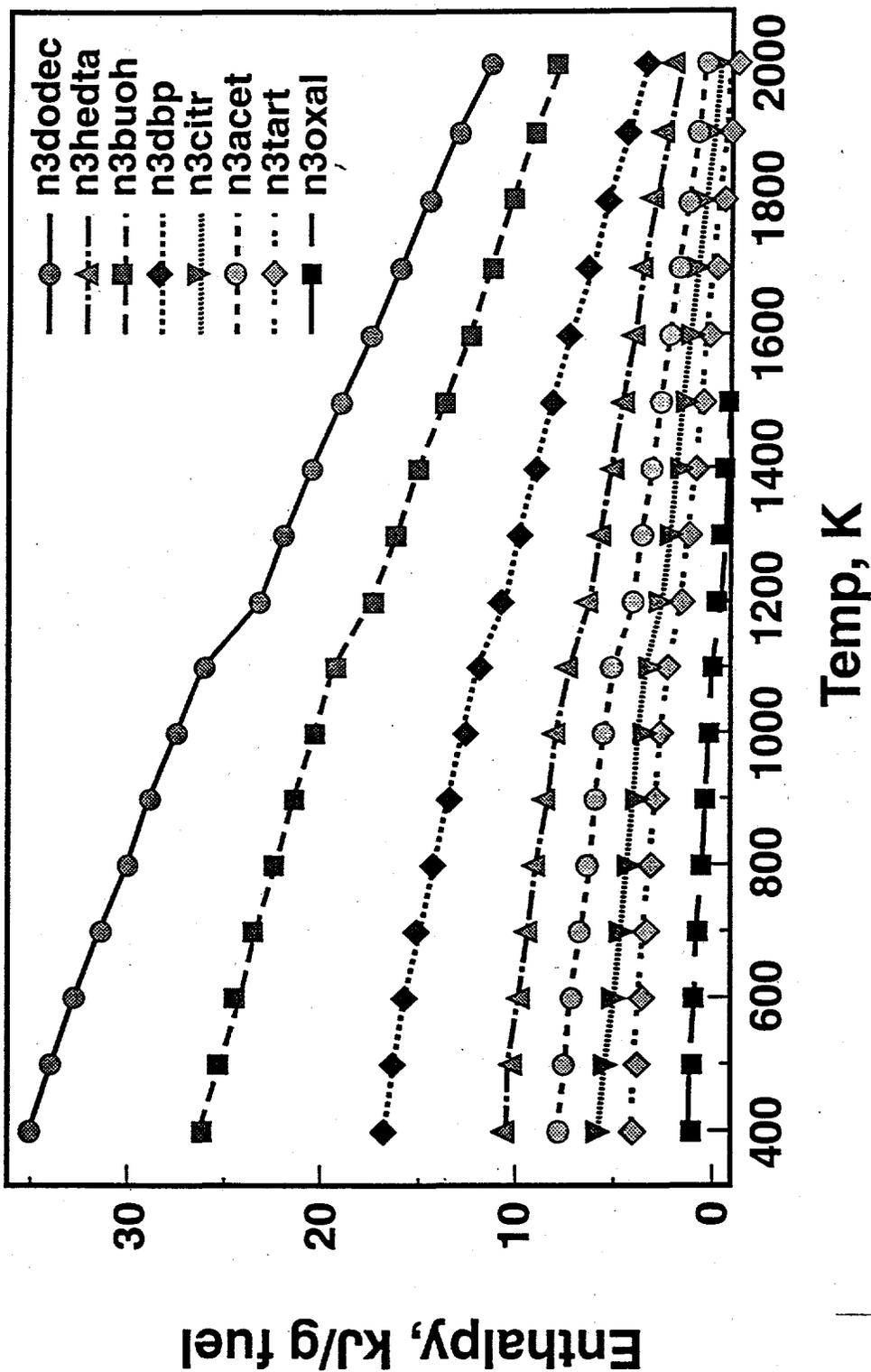
A concentrated caustic solution is expected to be the last aqueous phase to disappear as a waste is heated. Its high effective heat capacity results from the negative of the heat of solution, the vaporization of water, the melting of NaOH, and ultimately the vaporization of NaOH. Estimated total enthalpy values for 60 wt% NaOH are shown in Table 4.5 and Figure 4.5.

One of the more important questions concerns the fraction of water in the reactive mix and the temperature at which it is released. The portion as hydrates (including concentrated NaOH solution) is not normally removed at 373 K (100°C). It will be removed at a higher temperature and with a higher energy requirement. Analcite is used as a representative of a hydrated material. Its effective heat capacity resulting from the dehydration reaction is shown in Figure 4.6, which compares the enthalpy with and without water loss. The lower curve assumes no water loss from the compound. It would seem reasonable that hydrate water might make up 5 to 10 wt% at the time an exothermic reaction



S9406007.14B

Figure 4.3. Comparison of Heats of Reaction (Available Energy) with System Enthalpies



S9406007.12B

Figure 4.4. Available Energy of Organic Compounds to 2000 K. Compounds are sodium salts except for butyl alcohol (buoh).

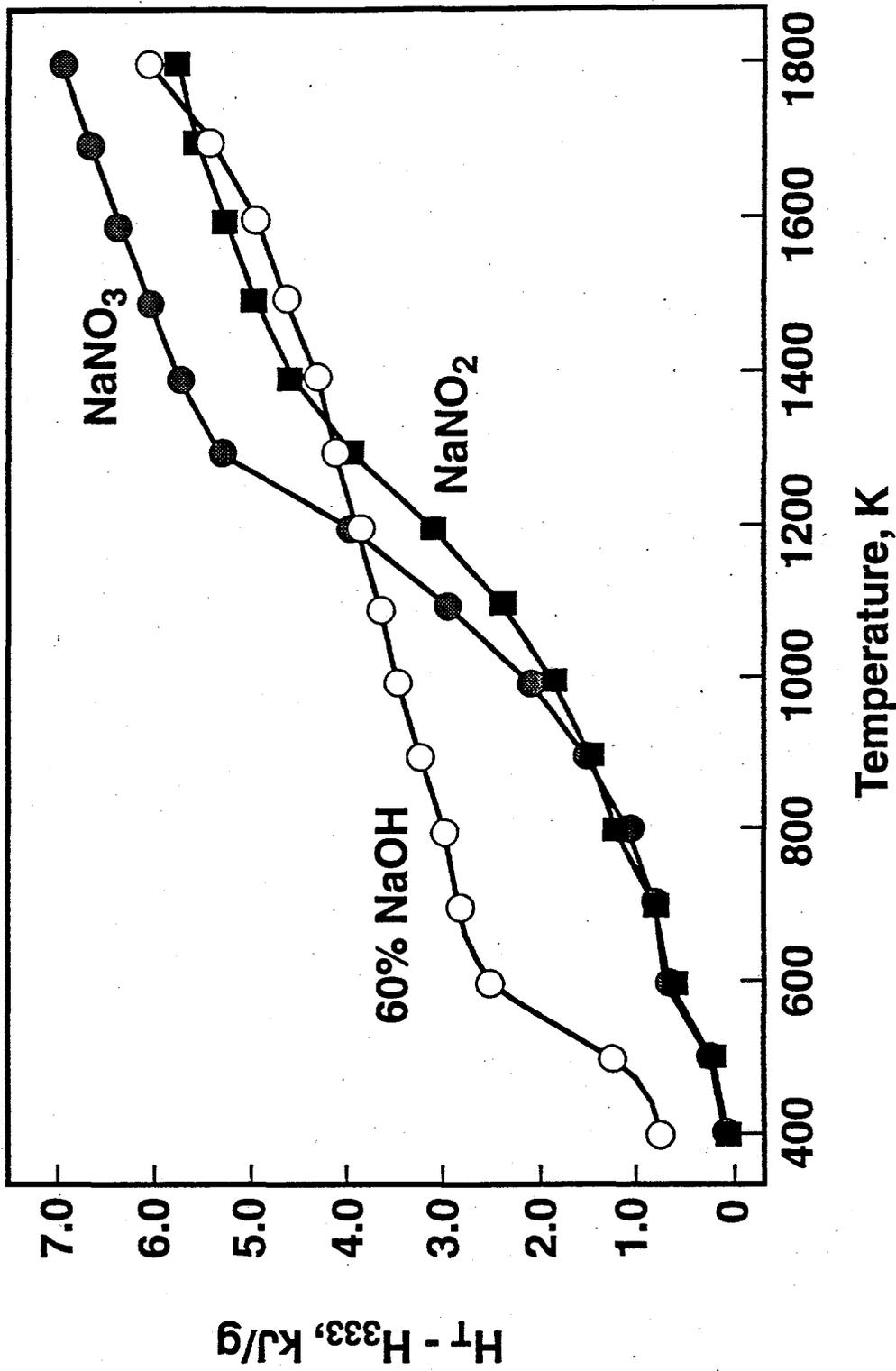
Table 4.4. Energy Required to Heat an Arbitrary Mix to Different Temperatures

| Compound/g | Energy, J | | | | | | | |
|---------------------------------|-----------|-------|-------|-------|-------|-------|--------|-------|
| | 400 K | 500 K | 600 K | 700 K | 800 K | 900 K | 1000 K | |
| NaNO ₃ | 1.0 | 85.4 | 235.6 | 639.7 | 824 | 1,004 | 1,188 | 1,372 |
| NaNO ₂ | 0.5 | 39.7 | 111.7 | 304.6 | 393 | 481 | 569 | 657 |
| NaAlO ₂ | 1.0 | 66.1 | 172.4 | 283.7 | 402 | 536 | 657 | 778 |
| Na ₂ CO ₃ | 1.0 | 76.1 | 202.1 | 345.6 | 510 | 665 | 816 | 979 |
| H ₂ O | 0.2 | 498.7 | 535.6 | 577.4 | 619 | 661 | 703 | 749 |
| Total | | 770 | 1,255 | 2151 | 2749 | 3,347 | 3,933 | 4,535 |

Table 4.5. Estimated High-Temperature Enthalpy Data for NaNO₃, NaNO₂, and 60% NaOH, J/g

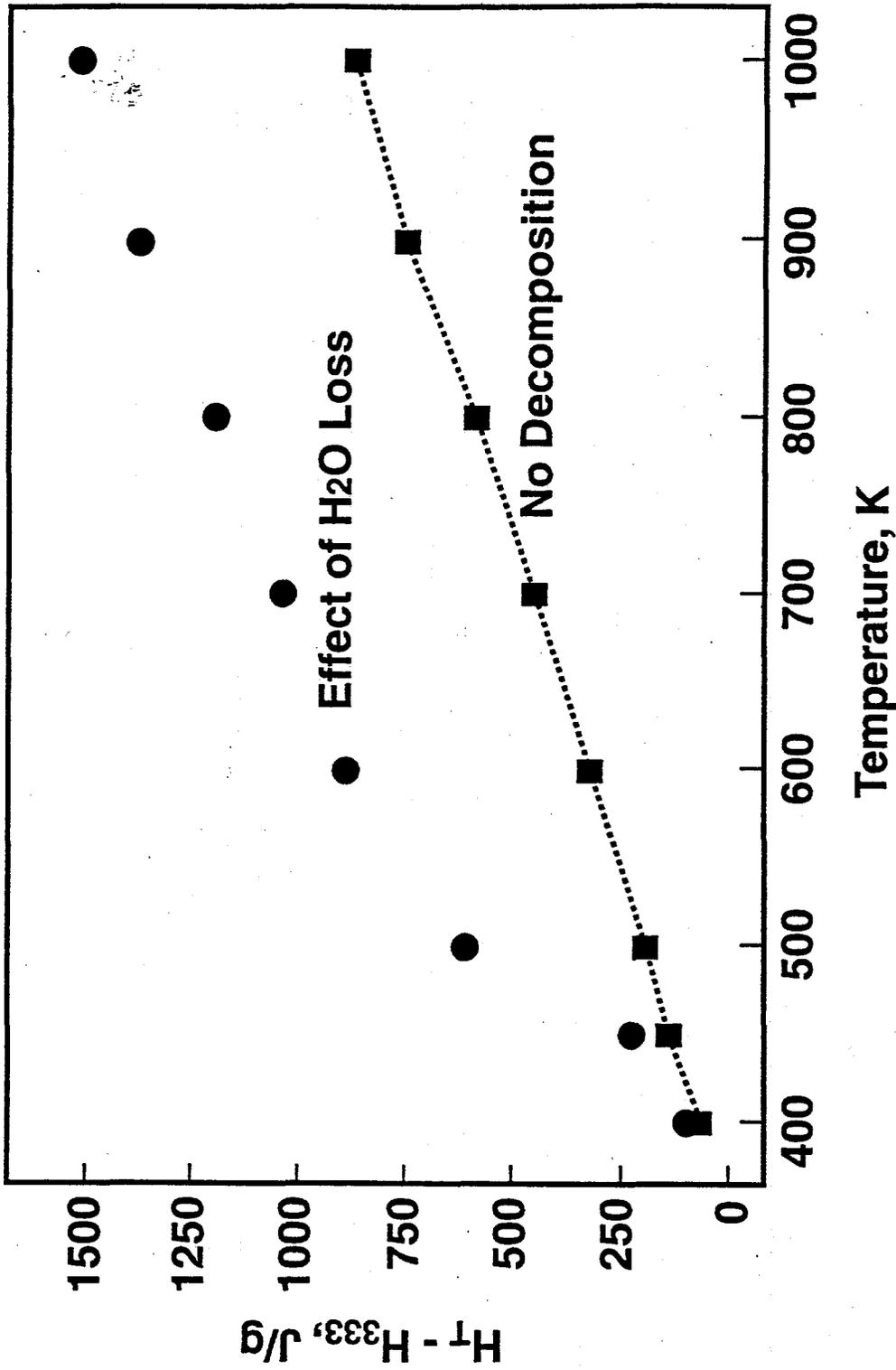
| Temperature, K | H _T -H ₃₃₃ | | |
|----------------|----------------------------------|-----------------------|--------------|
| | 1 g NaNO ₃ | 1 g NaNO ₂ | 1 g 60% NaOH |
| 400 | 84 | 79 | 732 |
| 500 | 234 | 222 | 1,745 |
| 600 | 640 | 607 | 2,573 |
| 700 | 782 | 795 | 2,782 |
| 800 | 1,059 | 1,184 | 2,992 |
| 900 | 1,515 | 1,460 | 3,201 |
| 1000 | 2,079 | 1,870 | 3,431 |
| 1100 | 2,933 | 2,393 | 3,640 |
| 1200 | 3,975 | 3,079 | 3,849 |
| 1300 | 5,209 | 3,895 | 4,088 |
| 1400 | 5,728 | 4,506 | 4,310 |
| 1500 | 6,012 | 4,904 | 4,602 |
| 1600 | 6,318 | 5,188 | 4,937 |
| 1700 | 6,623 | 5,481 | 5,397 |
| 1800 | 6,912 | 5,732 | 6,004 |

starts, and as noted earlier may represent an effective heat capacity 50% to 100% greater than the same mass of pure water. The uncertainty here will be narrowed with identification of actual tank constituents and by thermal analysis experiments under way at the Pacific Northwest Laboratory and elsewhere.



R9508095.2

Figure 4.5. Estimated High Temperature Enthalpy



R9508095.3

Figure 4.6. Enthalpy of Analcite

Finally, it is instructive to consider a more realistic energy release from the nitrate/nitrite reactions. We know that NO is produced in some reactions and may escape (Scheele et al. 1992; Burger and Scheele 1991). If 30% reacted to produce NO, the net energy release for the ferrocyanide-nitrate/nitrite reaction would be 6.28 kJ/g at 500 K and 5.23 kJ/g at 1000 K, in place of 9.51 and 7.37 kJ/g, respectively, found for the most efficient reaction. In many reactions N_2O is a product. The effect on the reaction enthalpy was tabulated for numerous compounds in Tables 3.1 to 3.3.

The figures illustrate the many relations that can be represented using data from Tables 4.1 and 4.2 and enthalpy tables in the appendix.

The maximum adiabatic temperatures discussed here are conventionally calculated by equating the equation for the heat of reaction as a function of temperature to the heat capacity equation for the system. However, it is more informative to display the data graphically as a function of temperature, as in Figure 4.3.

An alternative presentation is the triangular diagram used by Colby and Crippen (1992). In this, the reactive region can be displayed using, for example, the parameters fraction water and fraction inert material for a given mix of fuel and oxidant.

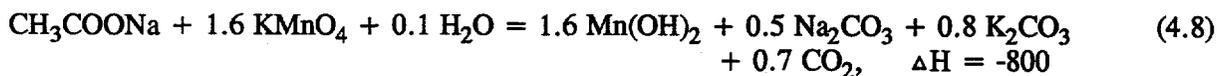
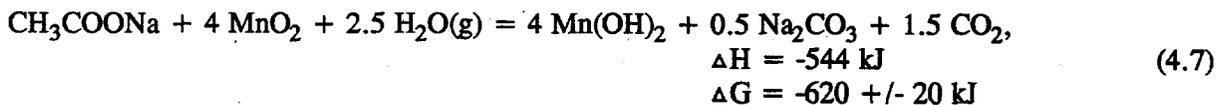
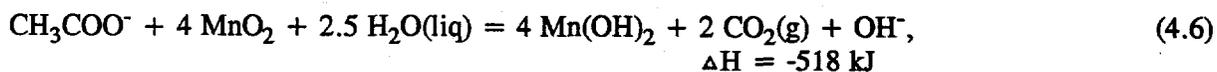
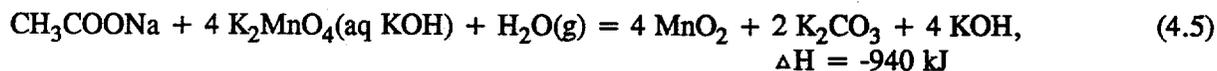
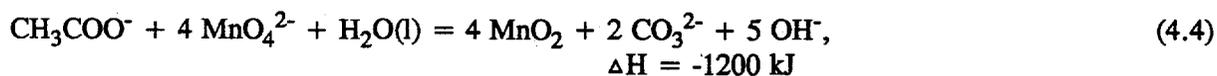
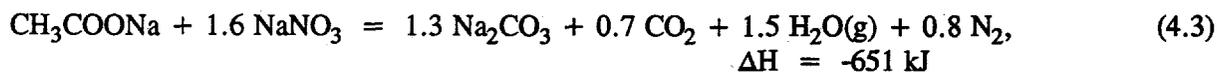
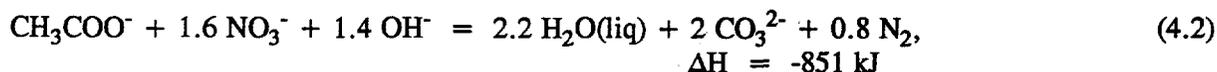
4.3 High-Temperature Reactions

At lower temperatures loss of free water or hydrate water is a major heat sink. Above about 1000 K, other reactions that raise the heat capacity of the system become significant. The most important of these reactions are predicted to be the thermal decomposition of $NaNO_3$ and $NaNO_2$. Assuming 10% decomposition at 900 K, 40% at 1100 K, and 100% at 1400 K, the data for $H_T - H_{333}$ for $NaNO_3$ and $NaNO_2$ are estimated and listed in Table 4.5. The data include a small additional enthalpy for vaporization, 10% at 1200 K and 40% at 1800 K. Neglecting this correction would lower the enthalpies about 5% at 1200 K and 15% at 1800 K. Equilibrium data would predict a greater effect than shown, but the slow rate of decomposition would tend to reduce it. Thus, the data must be considered to be very rough estimates of what might be an *effective* enthalpy. Estimated data for a 60% (near saturation at 333 K) solution of NaOH are included in the table. The data were included in Figure 4.5. The numbers have a large uncertainty, several hundred J-per gram at the higher temperatures. Discrete data for the nitrate and nitrite are hypothetical since, as noted earlier, a pseudo-equilibrium is approached at temperatures a few hundred degrees above the melting point, about 508 K for the eutectic. Thus, a realistic value for either compound may lie between the two curves, with an uncertainty of about 400 J/g at 1000 K and 1200 J/g at 1800 K. In spite of the uncertainty, the numbers are so large that production of extremely high temperatures in the presence of excess nitrate or nitrite is not likely.

4.4 Other Oxidants

It is necessary to consider whether oxidants other than nitrates and nitrites might be important. Other oxidants include Cr and Mn compounds; both elements may be present in appreciable amounts. Manganese was used in the form of permanganate as an oxidant in the Bismuth Phosphate Process. The same compound aided solvent washing for PUREX. It is reasonable to assume that the relatively small amounts used would survive in the alkaline waste tanks in the form of MnO_2 , although the exact form of this rather complex solid is unknown. The recent indication that large amounts of manganese may exist in one or more waste tanks suggests a re-examination of Mn reactions. It is not likely that the 7, 6, and 5 oxidation states would have survived 20 to 30 years in waste tanks, but the 6 and possibly the 5 states cannot be completely dismissed at least where reaction intermediates are concerned.

Oxidation of organic compounds by permanganate, manganate, or manganese dioxide produces a surprisingly high theoretical energy release. The following reactions are examples. Both ionic and nonionic reactions were calculated at 298 K and compared to the nitrate reactions.

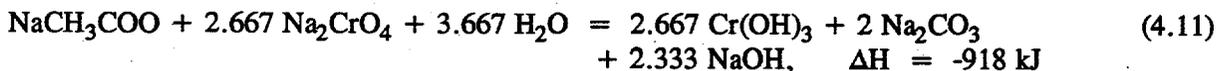
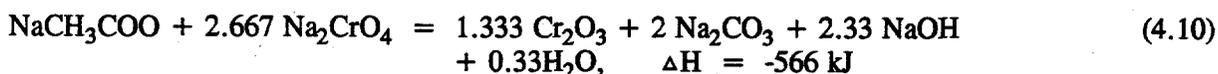
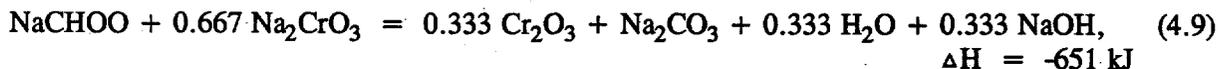


The reference states are crystalline for nonionic, and infinite dilution for ionic species except as indicated.

Producing MnO_2 in place of Mn(OH)_2 in the permanganate reactions will add +68 kJ to the calculated values. Several permanganate reactions were calculated but they are not considered plausible since the existence of Mn(VII) in the waste tanks is not expected. Instead, reactions similar to (4.6) and (4.7) are the likely possibilities. The stable manganese compound in an alkaline environment is MnO_2 . However, it is still a good oxidizing agent. It is converted to Mn_2O_3 , Mn_3O_4 , and MnO , in that order, as the temperature is raised. The calculated partial pressure of O_2 over MnO_2 is about 40 torr at 400°C . Determining the effectiveness of the compound (kinetically) as an oxidant of the tank constituents at low temperatures requires experimentation. There is little doubt that reactions like (4.6) or (4.7) will occur as the temperature is raised. Thus appreciable manganese in the waste tanks will increase the available energy if sufficient organic compounds are available.

The other issue of a concern is a possible catalytic effect. MnO_2 is an effective catalyst for many oxidation reactions. The mechanism for catalysis of nitrate oxidation is assumed to be $\text{Mn}(+4) \rightarrow \text{Mn}(+6)$, with the nitrate reduced to nitrite. The $\text{Mn}(+6)$ as oxide decomposes to $\text{Mn}(+4)$ plus oxygen (Ephraigm, 1953). This explanation, $\text{MnO}_2 \rightarrow \text{MnO}_3$, may be too simple since a high positive free energy is involved as written. Also, MnO_3 probably does not exist as a compound (Bailar, 1973). Regardless, MnO_2 is known to be a catalyst and deserves a few experiments, e.g., MnO_2 added to nitrate-oxidation DSC experiments.

Dichromate was used in the REDOX process, and would exist as chromate in the waste. Although Cr(III) is the expected from after storage some Cr(VI) may have survived several calculations are included here. Examples of possible reactions are:



It is interesting to note that the free energy for the formation of chromate from Cr_2O_3 in a basic system in the presence of a small amount of oxygen is highly negative. The equilibrium constant using sodium carbonate as reactant,

$$K = (\text{CO}_2)^2/(\text{O}_2)^{1.5} (\text{atm})^{1/2}, \quad (4.12)$$

is $1.2 \text{ E}15$ at 400 K, $1.5 \text{ E}13$ at 500 K, and $7.4 \text{ E}11$ at 600 K. This suggests that chromate could be a catalyst for the oxidation of organics in a basic system.

Table 4.6 lists calculated reaction enthalpies for several organic compounds.

It will be noted that the reaction energies with MnO_2 are somewhat less than with sodium nitrate, Table 4.1.

Table 4.6. Reaction Enthalpies with Different Oxidants

| Compound | - ΔH , kJ/mol Oxidant | | |
|-----------------------|---------------------------------|-----------------------|----------------------|
| | $\text{Na}_2\text{CrO}_4^{(a)}$ | $\text{KMnO}_4^{(b)}$ | $\text{MnO}_2^{(b)}$ |
| Na acetate | 918 | 800 | 544 |
| Na_2 oxalate | 270 | 205 | 140 |
| Na_3 citrate | 2196 | 1791 | 1306 |
| Na_4 EDTA | 4748 | 4101 | 2799 |
| C | 479 | 388 | 259 |
| CH_4 | 846 | 792 | 533 |
| Vinyl pyridine | 3972 | 3727 | 2283 |

(a) The product is $\text{Cr}(\text{OH})_3$.

(b) The product is $\text{Mn}(\text{OH})_2$.

4.5 Kinetics

The importance of the rates of decomposition on the effective enthalpy of diluents has been mentioned. The kinetics of the oxidation reactions themselves have not been discussed. This is a very complex problem, because the overall reactions may include independent thermal decompositions of the fuels and oxidants, in addition to the fact that many of the oxidation reactions may occur stepwise. Assuming that an exothermic reaction can be generalized, then the rate of heat production for one mol of reactant is given by

$$dH/dt = Z\Delta H \exp(-E_a/RT) \quad (4.13)$$

where Z is the pre-exponential, ΔH the enthalpy of reaction, and E_a the activation energy. For the units used here the dimensions are joules per mol-second. The rate of temperature rise, dT/dt , resulting from the heat produced, becomes inversely proportional to the specific heat plus a thermal conductivity term. The presence of the conductivity factor, which is time-dependent, increases the significance of E_a , which is already a very significant parameter.

A diagram first used by Semenov (Stull 1977) is useful in explaining ignition or runaway excursions resulting from exothermicity. In Figure 4.7, the curved line represents the rate of heating according to Reaction (4.13) for an arbitrary set of kinetic parameters. The rate of heat loss is given by the isothermal parallel lines. The latter temperatures are the surrounding temperatures, considered to be an infinite heat sink; i.e., a thermostat for an experimental set-up, or the surface of a test explosive. Points on these lines show the rate of heat loss.

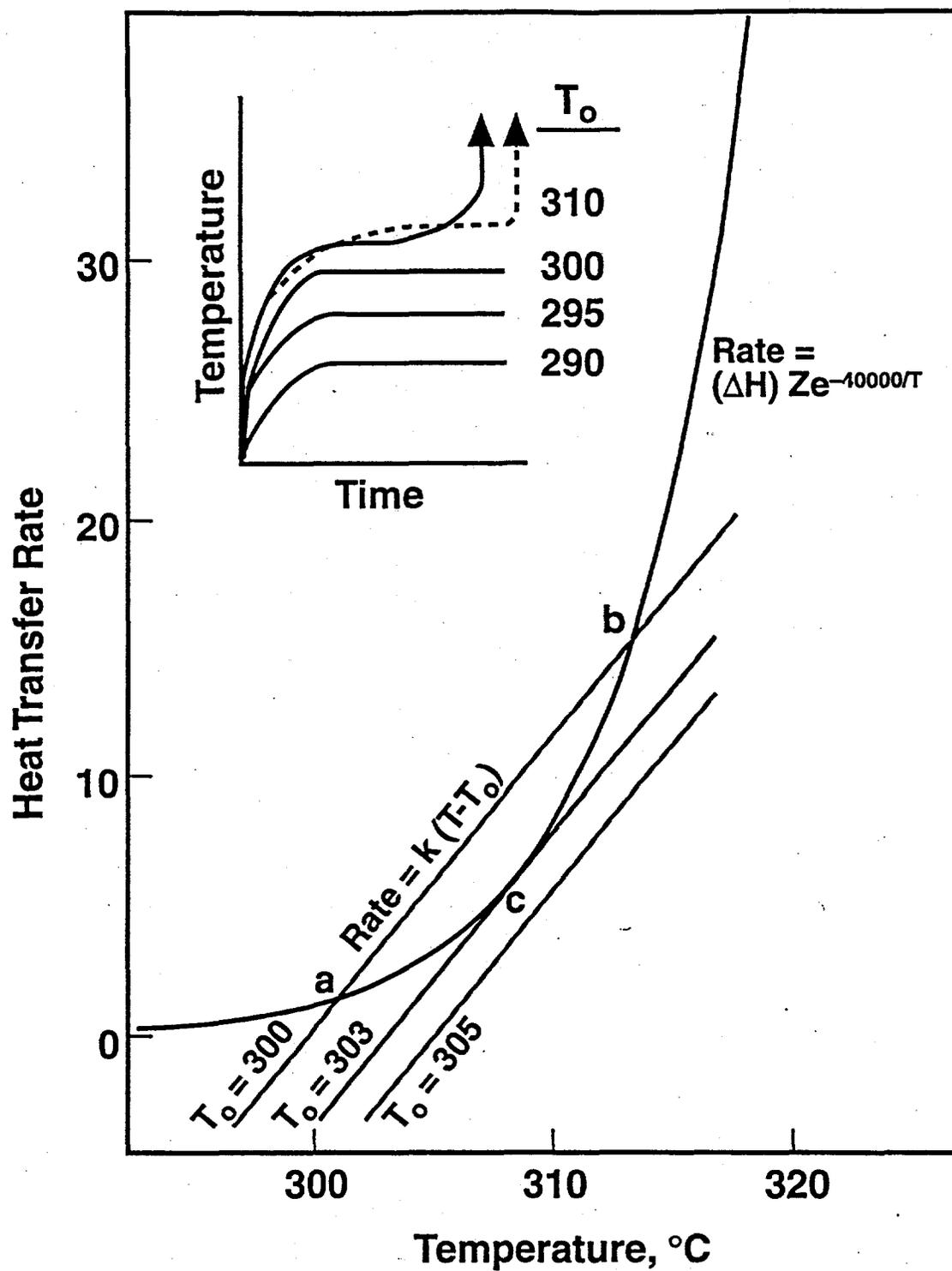
Referring to the figure, if the surrounding temperature is 300°C , then the chosen reaction would self-heat to point a, at which time the heat loss is equal to the production and no further heating takes place. At 303°C the temperature rises to about 308°C , where at point c the loss is again equal to the heat production. At a surrounding temperature of 305°C or greater the reaction heat cannot be removed and the reaction goes rapidly to explosive rates. At 300°C any rate of heating less than point b is removed to the surroundings and the reaction is self-controlled. The temperature-time plot in the figure shows typical temperature measurements of a sample placed in a thermostat at four different temperatures. The dashed line emphasizes that one cannot predict exactly when the ignition or explosion will occur, only that it will occur. In addition to the thermal conductivity, the size and shape of the reaction mixture sample become very important variables in the real world.

A thorough discussion of kinetics, including the induction period and the critical temperature for explosion, very important aspects of exothermic reactions, is beyond the scope of the present paper.

4.6 Maximum Adiabatic Temperatures

Of course, the right proportions of reactants and oxidants discussed here can theoretically produce very high temperatures, and under optimal conditions, violent explosions. The adiabatic temperature maximum for the ferrocyanide-nitrate reaction (100% efficiency) is estimated to be approximately 2200 K. In this case the temperature is limited by the decomposition of Na_2CO_3 , aided slightly by a 2200 K transition of NiO. If the system is not completely dry, the temperature limit will be considerably lower due to the heat capacity of water itself and to the concomitant volatilization of NaOH.

With NaCH_2COO the maximum temperature reached with the NaNO_3 reaction is calculated to be about 2000 K. With NaDBP the temperature is probably about 2200 K to 2300 K. The behavior of Na_3PO_4 as a heat sink at these temperatures is uncertain. Again, it is emphasized that these estimates are for 100% efficient reactions. The maximum temperatures would be reached with very fast reactions, e.g., explosions. The same behavior is seen with high explosives. Decomposition of pentaerythritol tetranitrate (PETN) or hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), for example, by impact or by slow heating, creates large amounts of NO and N_2O in place of N_2 and thus produces a



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Figure 4.7. Prediction of Thermal Excursions

lower energy release than is obtained on explosion (Bowden and Yoffe 1949). As mentioned earlier, the explosive reactions themselves are commonly about 80% efficient. Heat loss by thermal conductivity and thermal radiation will always be finite and further reduce the actual temperature reached.

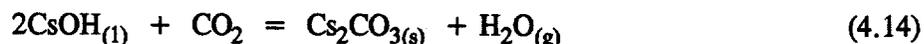
Delayed explosions, sometimes for several hours, are a characteristic of reactive mixes of the type examined here when placed in a high-temperature environment. These are illustrated by the time-to-explosion tests of cyanide-nitrate/nitrite systems (Scheele et al. 1992) and the reaction of NaCH_3COO with NaNO_3 (Kozlowski and Bartholomew 1968). Temperatures in the vicinity of 600 K to 650 K are usually adequate to produce explosive reactions.

As noted earlier, diluents have a very significant effect. The addition of 1.0 g of an inert substance such as Na_2SO_4 to the NaCH_3COO mix (1 g of NaCH_3COO fuel) lowers the maximum temperature from 2000 K to 1600 K. The same quantity of a high heat-capacity material such as NaOH would have nearly twice the effect. If the NaOH is in solution, the effect is greater yet.

4.7 Volatilization of Salts

Since excess nitrate/nitrite salts are most certainly present in excess of *fuel* in the waste tanks along with inert compounds, this exercise suggests that temperatures most likely would not rise to the point where aerosol formation from vaporization occurs.

However, while calculations from free-energy data show the vapor pressure of NaOH to be about 1 torr at 1200 K, by a similar calculation for CsOH we find 380 torr (free-energy data from Barin 1989). Cesium oxide, less volatile, is not a likely product since some water vapor will always be present. However, Cs_2CO_3 must be considered since CO_2 is a major reaction product. As with the sodium analog, it is stable to high temperatures (the free energy for the reaction converting the hydroxide to the carbonate at different temperatures is uniformly about 25 kJ/mol more negative for cesium than for sodium). For the reaction



the free energy at 1000 K is -103 ± 5 kJ, giving an equilibrium constant, K_{eq} , of $2.4 \text{ E}05$. At 1200 K, K_{eq} is about 500 and at 1300 K about 50 to 100. The vapor pressure of CsOH will be

$$P_{\text{CsOH}} = [(\text{H}_2\text{O}/\text{CO}_2)(1/K_{eq})]^{1/2} \quad (4.15)$$

The free-energy data suggest that unless the $\text{H}_2\text{O}/\text{CO}_2$ ratio is much greater than unity, cesium would not vaporize at 1200 K to 1300 K. In a dry system cesium should remain as the carbonate at even higher temperatures. Thus, if a reasonably concentrated cesium mixture were present at the reactive

site, then the possibility of volatility may depend on the water content and on which reactions go to completion, and of course, on the temperature. In addition, these calculations ignore the thermodynamic activities. The composition of the actual liquid phase following a rapid exothermic reaction is unknown. It is likely that only experimental work can answer this question of cesium volatility. Equilibrium data for the CsOH-CO_2 reaction are shown in Figure 4.8.

The instability and endothermic decomposition of $\text{NaNO}_3/\text{NaNO}_2$ may explain why we experimentally find explosions with ferrocyanide-nitrate/nitrite mixes in our time-to-explosion (TTX) tests for high $\text{FeCN}/\text{oxidant}$ ratios (up to 5:1) but not for high oxidant/ FeCN ratios (Scheele et al. 1991). This hypothesis requires that the ferrocyanide be kinetically more thermally stable than the nitrate or that it decomposes to intermediates with a low enthalpy change.

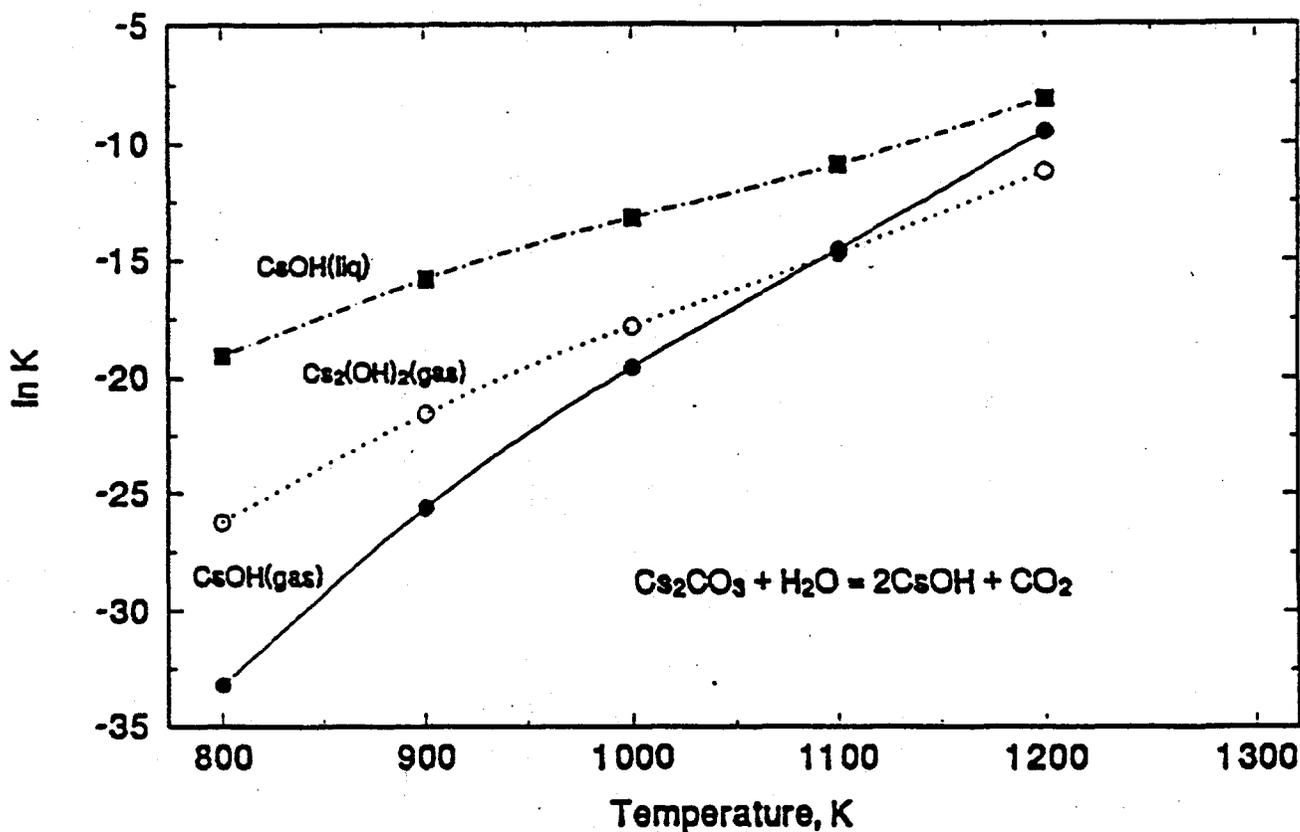


Figure 4.8. $\text{CsOH-Cs}_2\text{CO}_3$ Equilibrium

5.0 Summary and Conclusions

The reaction energies available from a variety of reactions of organic compounds and ferrocyanides have been compared for different temperatures. The relative effect of different *diluents* has been calculated as a function of temperature. The effect of excess oxidants and of diluents on the maximum temperature reached has also been calculated. Several figures are presented to illustrate how the data may be used. Gas production from various reactions is also presented.

There is a great difference among oxidizable compounds, *fuels*, in the energy available per gram of reactant (a factor of about 25) and a difference in the amount of energy per gram of reactant-oxidant mixture (a factor of about 5). Correspondingly, the amount of oxidant required for one gram of reactant also varies widely. This can be very significant since excess oxidant may be the most important heat sink after water is lost.

It is found that reaction energy predicted by carbon content is not very reliable. Other correlations were tested but none were very satisfactory. Consideration of each compound is important.

Different diluents were compared for their capability to limit reaction temperatures or to prevent the reaction from occurring. Water, free or as hydrates, is of course the most effective diluent. Several hydrates will retain water to well over 450 K, thus greatly increasing their effective heat capacity. A concentrated solution of NaOH behaves similarly, and still loses water at 575 K.

The energy required to remove water from a hydrate or from a NaOH solution is much greater than the heat of vaporization of pure water. Thus, in the range 400 K to 600 K, stable hydrates are seen as the most effective diluents for limiting the oxidation reactions. Above about 500 K the melting of inorganic salts becomes important. At about 750 K endothermic decomposition reactions begin to be important.

It is calculated that production of high temperatures is greatly limited by the highly endothermic decomposition of several salts such as NaNO_3 , NaNO_2 ; at higher temperatures, NaSO_4 ; and at still higher temperatures, Na_2CO_3 . Also, the heat capacity of compounds such as NaOH increases rapidly with temperature; the compound is especially effective if dissolved in a small amount of water. Volatility of several compounds also becomes significant and important as a heat sink at temperatures starting at about 1100 K.

Temperatures sufficient to form aerosols by vaporization of large amounts of inorganic compounds are considered unlikely. The exception may be that of cesium. Cesium hydroxide is exceptionally stable and can vaporize at temperatures above about 1150 to 1200 K. However, a small concentration of CO_2 could prevent this. Experiments are required to determine the fate of cesium.

As noted in the Introduction, the calculations in this study assume for the most part that reactions follow the lowest energy path (maximum reaction enthalpy) and that equilibrium exists where reactions are reversible. This is normally the high-temperature path. High-temperature reactions of the mixtures examined here often become delayed deflagrations, sometimes after several hours. However, low temperatures and the presence of diluents tend to minimize this. Under these conditions many reactions will not go to completion, or they may follow a higher energy path, leaving a kinetically stable but high-energy species.

Only experimental investigation of mechanisms can determine the significant species and the critical reactions; then it can be determined whether a potentially reactive waste is hazardous, and if so, how it can be converted to a more benign state.

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Appendix

Thermodynamic Data

Appendix

Table A.1. Thermodynamic Properties of Significant Compounds, 298 K

| Compound | | ΔH_f , kJ/mol | ΔG_f , kJ/mol | C_p , J/mol-K | Reference ^(a) |
|---------------------------------|-----|-----------------------|-----------------------|-----------------|--------------------------|
| O ₂ | g | 0 | 0 | 29.36 | |
| H ₂ | g | 0 | 0 | 28.82 | |
| H ₂ O | g | -241.82 | -228.57 | 33.58 | |
| H ₂ O | liq | -285.83 | -237.13 | 75.29 | |
| H ₂ | g | 0 | 0 | 28.82 | |
| N ₂ | g | 0 | 0 | 29.12 | |
| NO | g | 90.25 | 86.55 | 29.84 | |
| NO ₂ | g | 33.18 | 51.31 | 37.20 | |
| N ₂ O | g | 82.05 | 104.2 | 38.45 | |
| SO ₂ | g | -286.22 | -300.19 | 39.87 | |
| SO ₃ | g | -389.99 | -371.06 | 50.67 | |
| H ₂ S | g | -20.63 | 33.56 | 34.23 | |
| NH ₄ NO ₃ | cr | -365.56 | -183.87 | 139.3 | |
| NH ₃ | g | -46.11 | -16.45 | 35.06 | |
| NTA | cr | -1307 | | | do |
| EDTA | cr | -1759.4 | | | do |
| HEDTA | cr | (-1552) | | | |
| DETPA | cr | -1570.5 | | | do |
| C | cr | 0 | 0 | 8.51 | |
| CH ₄ | g | -74.81 | -50.72 | 33.76 | |
| CO | g | -110.52 | -137.17 | 29.14 | |
| CO ₂ | g | -393.51 | -394.36 | 37.11 | |
| CH ₃ OH | liq | -238.66 | -166.27 | 81.6 | |
| HCOOH | liq | -424.72 | -361.35 | 99.04 | |
| HCOOH | g | -378.57 | | | |
| NaHCOO | cr | -666.5 | -599.9 | 82.68 | |
| HCHO | g | -108.57 | -102.53 | 35.40 | |

Table A.1. (contd)

| Compound | | ΔH_f , kJ/mol | ΔG_f , kJ/mol | C_p , J/mol-K | Reference ^(a) |
|---|-----|-----------------------|-----------------------|-----------------|--------------------------|
| HCONH ₂ | liq | -254.0 | | | |
| CO(NH ₂) ₂ | cr | -333.51 | -297.33 | 93.14 | |
| (CHO) ₂ glyoxal | g | -211.96 | | | |
| (COOH) ₂ | cr | -827.2 | | 117 | |
| CH ₃ CHO | liq | -192.30 | -128.12 | | |
| CH ₃ CHO | g | -166.19 | -128.86 | 57.3 | |
| CH ₃ COOH | liq | -484.5 | -389.9 | 124.3 | |
| CH ₂ OHCOOH | cr | -664.0 | | | |
| CH(OH) ₂ COOH | liq | -835.5 | | | |
| (CH ₃) ₂ NNO | liq | 4.6 | | | |
| C ₆ H ₈ O ₇ citric | cr | -369.0 | | | |
| n-decane | liq | -301.0 | 17.68 | 314.5 | |
| Sucrose | cr | -2225.5 | | | |
| NCCN | g | 308.95 | 297.36 | 56.82 | |
| HCN | g | 135.1 | 124.7 | 35.86 | |
| NH ₂ CN | cr | 59.0 | | | |
| (CH ₃) ₂ NH | g | -43.9 | 70.9 | 137.7 | |
| NH ₂ COCOOH oxamic acid | cr | -671.1 | | | |
| oxamide | cr | -514.6 | | | do |
| CH ₃ CONH ₂ | cr | -318.0 | | 67 | |
| NH ₂ CH ₂ COOH | cr | -528.10 | -368.44 | 99.20 | |
| C ₇ H ₇ N vinyl pyridine | liq | -155.6 | | | do |
| C ₄ H ₉ OH | liq | -327.4 | | | |
| NiS | cr | -82.0 | -79.5 | 47.11 | |
| FeO | cr | -272 | | | |
| Fe _{0.997} O | c | -266.27 | -245.12 | 48.12 | |
| Fe ₂ O ₃ | cr | -824.2 | -742.2 | 103.85 | |
| Fe(OH) ₃ | cr | -823.0 | -696.5 | | |
| Fe ₄ (Fe(CN) ₆) ₃ | cr | 1184 | | | |
| Fe ₂ CO(CN) ₅ | cr | 414 | | | |

Table A.1. (contd)

| Compound | | ΔH_f , kJ/mol | ΔG_f , kJ/mol | C_p , J/mol-K | Reference ^(a) |
|--|-----|-----------------------|-----------------------|-----------------|--------------------------|
| H ₄ Fe(CN) ₆ | cr | 426.8 | | | |
| Fe ₃ O ₄ | cr | -1118.4 | -1015.4 | 143.43 | |
| NiO | cr | -239.7 | -211.7 | 74.31 | |
| Na ₂ O | cr | -414.22 | -375.46 | 69.12 | |
| NaOH | cr | -425.61 | -379.49 | 59.54 | |
| Na ₂ SO ₄ | cr | -1387.08 | -1270.16 | 128.2 | |
| NaNO ₂ | cr | -358.65 | -284.55 | | |
| NaNO ₃ | cr | -467.85 | -367.00 | 92.88 | |
| TBP | liq | -1456 | | | bu |
| NaDBP | cr | (-1500) | | | |
| Na ₃ PO ₄ | cr | -1917.40 | -1788.80 | 153.47 | |
| Na ₂ NiFe(CN) ₆ | cr | (0.0) | | | |
| Na ₂ CO ₃ | cr | -1130.68 | -1044.44 | 112.30 | |
| HCOONa | cr | -666.5 | -599.9 | 82.68 | |
| NaHC ₂ O ₄ | cr | -1082 | | | |
| Na ₂ C ₂ O ₄ | cr | -1318 | | | |
| NaHC ₂ O ₄ -H ₂ O | cr | -1384.1 | | | |
| NaCH ₃ COO | cr | -708.81 | -607.18 | 79.0 | |
| NaCH ₂ OHCOO | cr | -900.8 | | | |
| NaCH(OH) ₂ COO | cr | -1082.0 | | | |
| Na ₃ C ₆ H ₅ O ₇ | cr | (-2260) | | | |
| Na ₄ EDTA | cr | (-2715) | | | |
| NH ₂ CH ₂ COONa | cr | -710.0 | | | |
| NaCN | cr | -90.75 | | | |
| NaCNO | cr | -405.39 | -358.1 | 86.6 | |
| NaNH ₂ COO | cr | -894.1 | | | |
| NaAlO ₂ | cr | -1135.12 | -1071.32 | 73.3 | |
| NaAlSiO ₄ nepheline | cr | -2092.8 | -1978.1 | | ba |
| NaAlSi ₂ O ₄ -H ₂ O analcite | cr | -3308.8 | -3082.6 | 209.9 | ba |

Table A.1. (contd)

| Compound | | ΔH_f , kJ/mol | ΔG_f , kJ/mol | C_p , J/mol-K | Reference ^(a) |
|----------------------------------|-----|-----------------------|-----------------------|-----------------|--------------------------|
| Al ₂ O ₃ | am | -1632 | | | |
| Cr ₂ O ₃ | cr | -1139.7 | -1058.1 | -118.7 | |
| Cr(OH) ₃ | cr | -1064 | | | |
| Na ₂ CrO ₄ | cr | -1342.2 | -1234.9 | 142.1 | |
| MnO ₂ | cr | -520.03 | -465.14 | 54.1 | |
| MnO | cr | -385.22 | -362.9 | 45.4 | |
| Analcite-dehydrated | cr | -2985.3 | | | ba |
| TNT | liq | -66.9 | | | dc |
| PETN | cr | -538.5 | | | dc |
| NH ₄ NO ₃ | cr | -365.56 | -183.87 | -139.3 | |

(a) Wagman et al. 1982, except bu-Burger (1988); ba-Barin (1989); dc-Dobratz and Crawford (1985); do-Domalski (1972). Estimated quantities in parentheses.

Table A.2. Heat Capacities of Compounds, C_p , J/mol-K^(a)

| Compound | | mol wt | 298.15 K | 400 K | 500 K |
|--|----|--------|----------|----------|---------------------|
| Al ₂ O ₃ | cr | 101.96 | 79.04 | 96.12 | 106.14 |
| C | cr | 12.01 | 8.51 | 11.93 | 14.63 |
| CCl ₄ | g | 153.82 | 83.40 | 91.69 | 96.61 |
| CH ₄ | g | 16.04 | 35.64 | 40.49 | 46.35 |
| C ₁₀ H ₂₂ | ℓ | 142.28 | 314.15 | 307.65 g | 359.80 g |
| CH ₂ O ₂ | g | 46.03 | 99.16 | 53.82 g | 61.06 g |
| CO | g | 28.01 | 29.14 | 29.34 | 29.79 |
| CO ₂ | g | 44.01 | 37.13 | 41.33 | 44.62 |
| Cs ₂ CO ₃ | cr | 325.82 | 123.83 | 136.37 | 145.77 |
| CsOH | cr | 149.91 | 67.87 | 74.39 | 82.42, 81.58 liq |
| FeO | cr | 71.85 | 49.94 | 51.81 | 53.45 |
| Fe ₂ O ₃ | cr | 159.69 | 103.87 | 120.12 | 131.81 |
| H ₂ | g | 2.02 | 28.84 | 29.18 | 29.26 |
| H ₂ O | ℓ | 18.02 | 75.29 | -- | -- |
| H ₂ O | g | 18.02 | 35.59 | 34.26 | 35.23 |
| MnO ₂ | cr | 86.94 | 54.42 | 63.49 | 67.99 |
| N ₂ | g | 28.01 | 29.12 | 29.25 | 29.58 |
| NH ₃ | g | 17.03 | 35.65 | 38.74 | 42.03 |
| NH ₄ NO ₃ ^(b) | cr | 80.04 | 139.03 | -- | -- |
| NO | g | 30.01 | 29.84 | 29.94 | 30.49 |
| NO ₂ | g | 46.01 | 36.66 | 40.90 | 43.67 |
| N ₂ O | g | 44.01 | 38.84 | 41.89 | 45.88 |
| NaAlO ₂ | cr | 81.97 | 73.03 | -- | -- |
| NaCN | cr | 49.01 | 50.18 | 51.95 | 53.17 |
| Na ₂ CO ₃ | cr | 105.99 | 111.03 | 125.02 | 142.35 |
| Na ₂ O | cr | 61.98 | 68.89 | 76.42 | 81.37 |
| NaOH | cr | 40.00 | 59.57 | 64.94 | 75.16 |
| NaOH•H ₂ O | cr | 58.02 | 90.17 | -- | -- |
| NaOH•3.5H ₂ O | ℓ | 103.07 | 128.02 | -- | -- |
| NaOH | g | 40.00 | 48.35 | 50.67 | 51.79 |

Table A.2. (contd)

| Compound | | mol wt | 298.15 K | 400 K | 500 K |
|--|----|--------|-----------|----------|-----------------------|
| Na ₃ PO ₄ | cr | 163.94 | 150.04 | 176.04 | 197.84 |
| Na ₂ SO ₄ | cr | 142.04 | 128.15 | 145.10 | 158.91 tr at 458 K |
| NaAlS ₁₂ O ₆ •H ₂ O | cr | 220.15 | 204.81 | 251.91 | 275.32 |
| NaAlS ₁₂ O ₆ | cr | 202.14 | 164.43 | 194.13 | 210.08 |
| O ₂ | g | 32.00 | 29.38 | 30.11 | 31.09 |
| SO ₂ | g | 64.06 | 39.90 | 43.36 | 46.66 |
| S ₁ O ₂ | cr | 60.08 | 44.58 | 53.43 | 59.64 |
| NaNO ₂ | cr | 69.00 | 69.01 | 89.00 | 108.07 |
| NaNO ₃ | cr | 85.00 | 92.88 | — | — |
| NaCH ₃ COO ^(c) | cr | 82.00 | 79.09 ± 2 | 120 ± 10 | 140 ± 15 |

(a) Data from Barin except as indicated.

(b) Wagman. (1992)

(c) Estimated using 298.15 K point of Wagman and scattered data from Gmelin, 21 Section 4 (1967). The mono hydrate is stable to 110°C.

Table A.3a. Enthalpy Data, $H_T - H_{333}$, J/g^(a)

| T, K | N ₂ | NO ₂ | C | N ₂ O | NH ₃ | H ₂ | O ₂ | NO |
|------|----------------|-----------------|--------|------------------|-----------------|----------------|----------------|--------|
| 300 | -34.32 | -27.82 | -28.47 | -29.67 | -70.99 | -470.23 | -30.24 | -32.42 |
| 400 | 69.83 | 56.94 | 57.87 | 61.28 | 147.27 | 971.23 | 62.59 | 67.04 |
| 500 | 174.85 | 149.01 | 168.69 | 161.13 | 384.44 | 2421.13 | 158.19 | 167.64 |
| 600 | 281.29 | 246.36 | 300.25 | 269.03 | 640.75 | 3874.01 | 256.94 | 270.44 |
| 700 | 390.07 | 348.03 | 448.29 | 337.51 | 915.67 | 5331.34 | 358.66 | 375.87 |
| 800 | 501.11 | 453.33 | 600.49 | 501.31 | 1208.22 | 6796.13 | 462.94 | 483.84 |
| 900 | 614.53 | 561.83 | 777.77 | 622.98 | 1517.26 | 8221.23 | 569.34 | 594.13 |
| 1000 | 730.00 | 673.14 | 954.20 | 747.21 | 1841.81 | 9761.41 | 677.53 | 706.51 |

(a) Wagman et al. 1982, except bu-Burger (1988); ba-Barin (1989); dc-Dobratz and Crawford (1985); do-Domalski (1972).

Table A.3b. Enthalpy Data, $H_T - H_{333}$, J/g^(a)

| <u>T, K</u> | <u>NaOH</u> | <u>Na₂O</u> | <u>Na₂CO₃</u> | <u>NaNO₃</u> | <u>NaNO₂</u> |
|-------------|-------------|------------------------|-------------------------------------|-------------------------|-------------------------|
| 300 | -48.87 | -37.82 | -35.10 | -37.74 | -34.73 |
| 400 | 105.77 | 80.04 | 76.07 | 85.48 | 80.08 |
| 500 | 279.91 | 175.27 | 201.92 | 235.35 | 223.34 |
| 548 | | | | 316.69 | |
| 548 | | | | 363.17 | |
| 557 | | | | | 317.69 |
| 557 | | | | | 534.17 |
| 572 | 424.17 | | | | |
| 572 | 604.09 | | | | |
| 579 | | | | 418.94 | |
| 579 | | | | 601.32 | |
| 596 | 656.64 | | | | |
| 596 | 821.91 | | | | |
| 600 | 830.52 | 342.04 | | 639.78 | 609.82 |
| 700 | 1044.91 | 482.12 | 510.99 | 822.87 | 784.17 |
| 800 | 1257.84 | 626.89 | 666.68 | 1005.92 | 961.53 |
| 900 | 1464.40 | 775.63 | 817.43 | 1189.01 | 1137.38 |
| 1000 | 1679.50 | 927.72 | 980.39 | 1372.10 | 1313.27 |

(a) Wagman et al. 1982, except bu-Burger (1988); ba-Barin (1989);
dc-Dobratz and Crawford (1985); do-Domalski (1972).

Table A.3c. Enthalpy Data, $H_T - H_{333}$, J/g^(a)

| T, K | <u>NaAlO₂</u> | <u>NaAlSiO₄</u> | <u>NaAlSi₂O₆*H₂O</u> | <u>Na₂SO₄</u> | <u>Na₃PO₄</u> |
|------|--------------------------|----------------------------|---|-------------------------------------|-------------------------------------|
| 300 | -31.05 | 28.16 | -33.14 | -30.96 | -31.38 |
| 400 | 66.02 | 64.10 | 72.26 | 65.56 | 68.53 |
| 500 | 172.26 | 171.13 | 192.46 | 174.47 | 182.67 |
| 514 | | | | 190.20 | |
| 514 | | | | 267.02 | |
| 600 | 283.97 | 275.93 | 321.08 | 317.75 | 309.62 |
| 700 | 399.66 | 385.51 | 455.22 | 497.18 | 448.73 |
| 740 | 446.85 | | | | |
| 740 | 462.67 | | | | |
| 800 | 534.30 | 499.82 | 593.54 | 626.76 | 599.73 |
| 900 | 655.88 | 618.81 | 0.00 | 760.94 | 762.49 |
| 1000 | 779.94 | 742.53 | 0.00 | 899.69 | |

(a) Wagman et al. 1982, except bu-Burger (1988); ba-Barin (1989); dc-Dobratz and Crawford (1985); do-Domalski (1972).

Table A.3d. Enthalpy Data, $H_T - H_{333}$, J/g^(a)

| <u>T, K</u> | <u>FeO</u> | <u>Fe₂O₃</u> | <u>NiO</u> | <u>NaCN</u> | <u>Fe(OH)₃</u> |
|-------------|------------|------------------------------------|------------|-------------|---------------------------|
| 300 | -23.10 | -22.30 | -23.68 | -45.35 | -32.76 |
| 400 | 47.74 | 48.16 | 40.63 | 94.81 | 70.92 |
| 500 | 121.04 | 127.19 | 117.15 | 235.14 | 187.74 |
| 600 | 196.44 | 212.76 | 196.10 | 375.60 | 314.47 |
| 700 | 273.72 | 303.84 | 267.69 | 516.22 | 449.32 |
| 800 | 352.63 | 400.24 | 339.11 | 657.01 | 591.03 |
| 835 | | | | 706.30 | |
| 836 | | | | 885.21 | |
| 900 | 433.132 | 501.95 | 410.66 | 991.06 | 738.48 |
| 1000 | 515.050 | 605.38 | 482.71 | 1,153.32 | 890.77 |

(a) Wagman et al. 1982, except bu-Burger (1988); ba-Barin (1989); dc-Dobratz and Crawford (1985); do-Domalski (1972).

Table A.3e. Enthalpy Data, $H_T - H_{333}$, J/g^(a)

| <u>T, K</u> | <u>H₂O(g ref)</u> | <u>H₂O(liq ref)</u> |
|-------------|------------------------------|--------------------------------|
| 300 | -61.55 | 2,304.51 |
| 400 | 126.57 | 2,492.62 |
| 500 | 319.32 | 2,685.42 |
| 600 | 517.85 | 2,883.91 |
| 700 | 722.74 | 3,088.80 |
| 800 | 934.20 | 3,300.26 |
| 900 | 1,152.69 | 3,518.74 |
| 1000 | 1,378.17 | 3,744.22 |
| 1100 | 1,610.84 | 3,976.89 |
| 1200 | 1,850.33 | 4,216.38 |
| 1300 | 2,096.60 | 4,462.65 |
| 1400 | 2,349.19 | 4,715.24 |
| 1500 | 2,607.76 | 4,973.81 |
| 1600 | 2,871.81 | 5,237.87 |

(a) Wagman et al. 1982, except
bu-Burger (1988); ba-Barin (1989);
dc-Dobratz and Crawford (1985);
do-Domalski (1972).