Freezing point lowering measurements were made on dilute solutions of NaCl, Na_2MoO_4, Na_2WO_4, KCl, and $BaCl_2$ in $NaNO_3$. Graphs of our experimental ΔT values against the corresponding molalities were straight lines whose slopes yielded the values of iK_f given in Table II with derived values for the heat of fusion of $NaNO_3$.

The "best" value for the heat of fusion of $NaNO_3$ calculated from our results is 3600 ± 100 cal./mole.

Freezing point depression measurements were also carried out on dilute solutions of KCl in KNO_3. The slope of the straight line in a graph of ΔT against m led to K_f = 23.9° C. per mole of foreign ions and ΔH_1 = 3080 cal./mole for the heat of fusion of KNO_3.

DISCUSSION

Equation 1 is valid only for dilute solutions from which the pure major component is frozen out as the temperature is lowered. We found no evidence for solid solution formation in any of the systems discussed in this paper.

Perman (*9*) made a few freezing point measurements in the $NaNO_3$-rich region of the $NaNO_3$-NaCl system. Nyankovskaya (*7*) studied the NaCl-$NaNO_3$-KCl-KNO_3 system over wide ranges of composition and temperatures. Our results are in good agreement with results of these earlier workers, although their data for dilute solutions are not precise enough to permit accurate evaluation of heats of fusion. Laybourn, Madgin, and Freeman (*6*) studied the $NaNO_3$-$Ba(NO_3)_2$ system and reported the eutectic temperature and composition to be 284° C. and 6.37 mole % $Ba(NO_3)_2$, in poor agreement with our results. Lifshits (*8*) reported that the system of KNO_3-KCl has an eutectic point at 320° C. (6 mole % KCl) and that the eutectic is composed of KNO_3 and $KNO_3 \cdot KCl$. He also reported a transition point at 360° C. (17.4 mole % KCl) with the solution composed of KCl and $KNO_3 \cdot KCl$. These conclusions are in agreement with our results.

The cryoscopic data of Van Artsdalen (*10*) lead to 3780 cal./mole for the heat of fusion of $NaNO_3$. Kelley (*4*) has recently reviewed the literature and listed the heat of fusion of $NaNO_3$ as 3490 cal./mole and in earlier reviews (*2, 3*) listed values from 3160 to 3800 cal./mole. Our value is 3600 cal./mole.

Table II. Freezing Point Constant and Heat of Fusion of $NaNO_3$

Minor Component	iK_f	ΔH_1, Cal./Mole
NaCl	15.7	3610 ± 100
Na_2MoO_4	16.0	3550 ± 100
Na_2WO_4	15.4	3700 ± 200
KCl	31.6	3600 ± 100
$BaCl_2$	50.2	3400 ± 250

In his recent review (*4*) Kelley has taken the heat of fusion of KNO_3 to 2800 cal./mole and earlier (*2*) listed values ranging from 2910 to 3040 cal./mole. Our value is 3080 cal./mole.

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Effect of Catalysts on Burning Rate of Ammonium Nitrate

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EARLY IN OUR efforts to determine the temperature profile and surface temperature of burning ammonium nitrate, a combustion catalyst was needed to get sustained combustion in a convenient pressure range. It introduced much "noise" in the temperature profile measurements; therefore an exploratory study was made on the effect of catalysts on the combustion of ammonium nitrate to determine the minimum catalyst concentration that would yield a system suitable for temperature profile measurements. This turned out to be 2.5% chromic oxide. The "noise" due to the catalyst particles seemed to be independent of particle size as long as they were less than 70 mesh (U. S. standard sieve). In the course of this brief study, some observations were made that may be of interest to investigators working in other fields.

EXPERIMENTAL

Reagent grade ammonium nitrate was used without further purification. It was ground to pass through a 200-mesh U. S. standard sieve and dried in a vacuum desiccator over Drierite. The ammonium dichromate was prepared similarly. Chromic oxide catalyst was obtained by thermal decomposition of ammonium dichromate. This chromic oxide was screened and only the fraction passing

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A brief comparative study was made on the catalytic effect of ammonium dichromate and chromic oxide on the burning rate of ammonium nitrate over the pressure range 68 to 306 atm. Some results on the effect of chromic oxide particle size are also given.

through a 200-mesh sieve was used for sample preparation. Usually the chromic oxide was used immediately after preparation; however, sometimes it was held in a desiccator for several days before use. The oxide was not analyzed for traces of dichromate ion. Only the top two-thirds of the oxide residue was selected and decomposition of the dichromate was assumed to be complete. It was found that commercial reagent grade chromic oxide had essentially no catalytic effect. Because of this it was assumed that the method of preparation of the catalyst was at least as important as its composition. No particle size measurements were made on any of the components.

Burning rate samples were sticks made of compressed powder. They were ¼ inch in diameter, and had a density of about 96% of theoretical. The sticks were then inhibited by dipping them in an acetone solution of cellulose acetate and allowing the solvent to evaporate. The samples were burned in a high-pressure, two-window combustion bomb which was pressurized with nitrogen. Burning rates were obtained by taking high-speed photographs of the burning strands with a Fastax camera. The details of this combustion apparatus have been described elsewhere (*2*). Burning rate curves were obtained for ammonium nitrate containing 3% ammonium dichromate and 1.5% and 3% chromic oxide over the pressure range 68 to 306 atm. The 68 atm. represents the lowest pressure at which sustained combustion took place; 306 atm. is near the safe pressure limit of the combustion bomb. Rate measurements were made at pressure intervals of about 34 atm. Usually two determinations were made at each pressure. Agreement between rates at a given pressure was about ±4% of the average value.

RESULTS AND DISCUSSION

In all cases the data showed a linear relation between log rate *vs.* log pressure. A least-squares fit of the data gave the following equations:

$$r = 4.67 \times 10^{-3} p^{0.96} \qquad \text{3\% ammonium dichromate}$$

$$r = 1.80 \times 10^{-3} p^{1.11} \qquad \text{1.5\% and 3\% chromic oxide}$$

where r is the rate in cm. per. sec. and p is the pressure in atmospheres. The two chromic oxide concentrations gave points that fell within experimental error of the same curve so that the burning rate is insensitive to the chromic oxide concentration in the region studied. Ammonium dichromate gave higher rates at all pressures than the equivalent concentration of chromic oxide. This is an interesting result since it is generally accepted that the real catalyst is chromic oxide and that it is effective in the vapor phase reactions (*1*). However, both catalysts gave burning rate equations with pressure exponents near unity. This would support the notion that the rate controlling reactions are the same in both cases and may be of second order. It is of interest to note that Andersen *et al.*, (*1*) obtained 0.65 for the pressure exponent for ammonium nitrate containing 3% ammonium dichromate. There is good agreement on the rate at 68 atm., however. Their pressure exponent is not in agreement with a second order rate controlling reaction. No obvious reason was found for this difference in pressure exponent. It may be related to the fact that Andersen's sample preparation was somewhat different and produced higher density specimens.

Only material passing through a 200-mesh sieve was used to obtain data for the above equations. But a brief study of the effect of catalyst particle size was made. It was found that particle size of the chromic oxide had some effect on burning rate. Generally 40 to 70-mesh particles gave burning rates higher than 70 to 100-mesh, and this gave higher rates than catalyst passing through a 200-mesh sieve. It is rather unlikely that the chromic oxide produced at the burning surface by thermal decomposition of ammonium dichromate had the same particle size distribution as the chromic oxide added to the mixtures. Consequently, the results obtained are somewhat ambiguous because of this effect.

Because the burning rate curves have slightly different slopes, it was of interest to see if they would cross or become the same curve. If the true catalyst were chromic oxide, the curves might be expected to become the same curve at high pressure. Over the pressure range studied the ammonium dichromate catalyst produced higher burning rates. This may be due to exothermic decomposition of ammonium dichromate near the burning surface. If this were the case the burning rate curves should never cross or even become the same curve. Unfortunately, our apparatus limitations made it impossible to verify this conclusion experimentally.

During these studies it was possible to confirm the observations of Andersen that nitrogen dioxide is one of the products of the catalytic decomposition of ammonium nitrate vapor (*1*). Although no quantitative determination of nitrogen dioxide was made, appreciable amounts could be seen by direct observation of the combustion products at all pressures up to 306 atm. Also, strong tests for nitrous and nitric acids were obtained from condensate found on all surfaces of the bomb after combustion.

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