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SURVEY OF POTENTIAL VAPOR-PHASE EXPLOSIONS IN DAREX AND SULFEX PROCESSES

K. S. Warren

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

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K. S. Warren

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ABSTRACT

A survey of the thermodynamics and limits of flammability of gases expected when sodium-bonded stainless steel—clad reactor fuels are dissolved in dilute aqua regia or sulfuric acid showed that vapor-phase explosions are a definite possibility with the aqua regia system. Reactions of hydrogen with nitrogen oxides, NOCl, and Cl_2 are highly exothermic, and mixtures of the gases are explosive over wide concentration ranges. The Sulfex process, in which only hydrogen is evolved, apparently could be used without additional hazard if the sodium-water reaction could be contained.

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1.0 INTRODUCTION

The literature was surveyed and calculations were made to determine the possibility of gas-phase explosions during dissolution of stainless steel—containing reactor fuels by the Darex (1) and Sulfex (1) processes. The gases evolved in such aqueous dissolutions could conceivably produce combustible and even explosive compositions in the gaseous phase in the dissolver. For example, erroneous measurement of the quantities of nitric acid and hydrochloric acids in the Darex process might be followed by production of hydrogen gas. While only traces of hydrogen have been detected (1) during dissolution of stainless steel in an acid mixture initially 5 M HNO_3—2 M HCl, significant amounts have been observed (2) with other acid compositions, e.g., 4 M HNO_3—3 M HCl. In the latter case N_2O is also evolved. This prompted an inquiry into the degree of hazard associated with the handling of all possible binary combinations of nitrogen- and chlorine-bearing gases and their admixtures with hydrogen. Since some of the fuels are sodium-bonded, the gaseous products from sodium—aqua regia and sodium—sulfuric acid reactions are also of interest. Accordingly, standard state heats and free energies of reaction were computed for a number of gaseous reactions pertinent to the dissolvent systems mentioned. Limits of combustibility and kinetics of the reactions were also surveyed. The thermodynamic calculations can only point to potentially hazardous mixtures, of course, and will not predict the rates at which equilibria will be attained. The presence or absence of catalytic substances will predominantly affect the latter.

The hazardous reactions in which oxygen would participate, if present, were not included in this survey. The hydrogen-oxygen problem, for example, is well recognized and has been treated recently (3) with respect to the energy release during an explosion and the resulting damage to an SRE fuel core processing cell. One factor not mentioned in that report is that the shock wave equation utilized may be limited to the range of 7 to 47 ft, according to the experimentalists who applied the equation to their results (4).

Dissolution experiments are designed to take place at atmospheric pressures only; the upper temperature of interest is thus the normal boiling point of the dissolvent used. Perhaps the highest boiling material likely to be encountered is 8 M H_2SO_4 containing dissolved inorganic salts, which would boil at ~130°C.

A literature survey issued in 1959 dealt with the solubilities (5) of argon, chlorine, hydrogen chloride, nitric oxide, nitrogen, nitrogen dioxide, nitrous oxide, and oxygen in water, aqueous nitric acid, aqueous hydrochloric acid, and aqua regia. Only partial data on the rates of the gaseous reactions of interest at such moderately elevated temperatures are available. The thermodynamic treatment of the several reactions was limited to the temperature range 0 to 300°C, which encompasses all dissolvent boiling temperatures likely to be encountered.

The valuable constructive criticism contributed by L. M. Ferris, of the Chemical Technology Division, during preparation of this survey is acknowledged.

2.0 THERMODYNAMIC CALCULATIONS

Twelve reactions involving gases that might be produced by the dissolution of stainless steel fuels (some containing sodium) by the Darex and Sulfex processes were evaluated:

$$H_2 + N_2O \longrightarrow H_2O + N_2 \quad (1)$$

$$H_2 + 2\ NOCl \longrightarrow 2\ HCl + N_2 + O_2 \quad (2)$$

$$2\ H_2 + 2\ NO \longrightarrow 2\ H_2O + N_2 \quad (3)$$

$$4\ H_2 + 2\ NO_2 \longrightarrow 4\ H_2O + N_2 \quad (4)$$

$$H_2 + NO_2 \longrightarrow H_2O + NO \quad (5)$$

$$H_2 + Cl_2 \longrightarrow 2\ HCl \quad (6)$$

$$H_2 + 2\ NOCl \longrightarrow 2\ NO + 2\ HCl \quad (7)$$

$$Cl_2 + 2\ NO \longrightarrow 2\ NOCl \quad (8)$$

$$4\ H_2 + 2\ SO_2 \longrightarrow 4\ H_2O + S_2\ (g) \quad (9)$$

$$3\ H_2 + SO_2 \longrightarrow 2\ H_2O + H_2S \quad (10)$$

$$4\ H_2S + 2\ SO_2 \longrightarrow 4\ H_2O + 3\ S_2\ (g) \quad (11)$$

$$2\ H_2S + 2\ NO \longrightarrow 2\ H_2O + N_2 + S_2\ (g) \quad (12)$$

Hydrogen could be produced directly from the dissolution of stainless steel or by reaction of sodium with water.

The enthalpy and free energy changes were derived from fundamental data taken from the literature. The heat capacity functions available from various sources (see Sect. 5.0) were used in calculations which yielded ΔH^o and ΔF^o as functions of temperature. Figures 1 and 2 show the temperature dependence over the range 0 to 300°C of (a) the standard-state heats, ΔH^o and (b) the standard free energies, ΔF^o, of reactions 1-12. The ΔF^o for all reactions except reaction 11, the H_2S-SO_2 reaction, was negative, indicating the thermodynamic possibility of the occurrence of these reactions under standard conditions. The ΔF^o is related to the equilibrium constant, K, by

$$\Delta F^o = -RT \ln K$$

from which it is obvious that the equilibrium constant is greater than unity when ΔF^o is less than zero. Any reaction with a negative ΔF^o is therefore thermodynamically favorable. The ΔH^o and ΔF^o values at 100°C (373°K) per gram-atomic weight of hydrogen, or equivalent, for reactions 1-12 are tabulated in Tables 1 and 2 according to the numerical size of the value.

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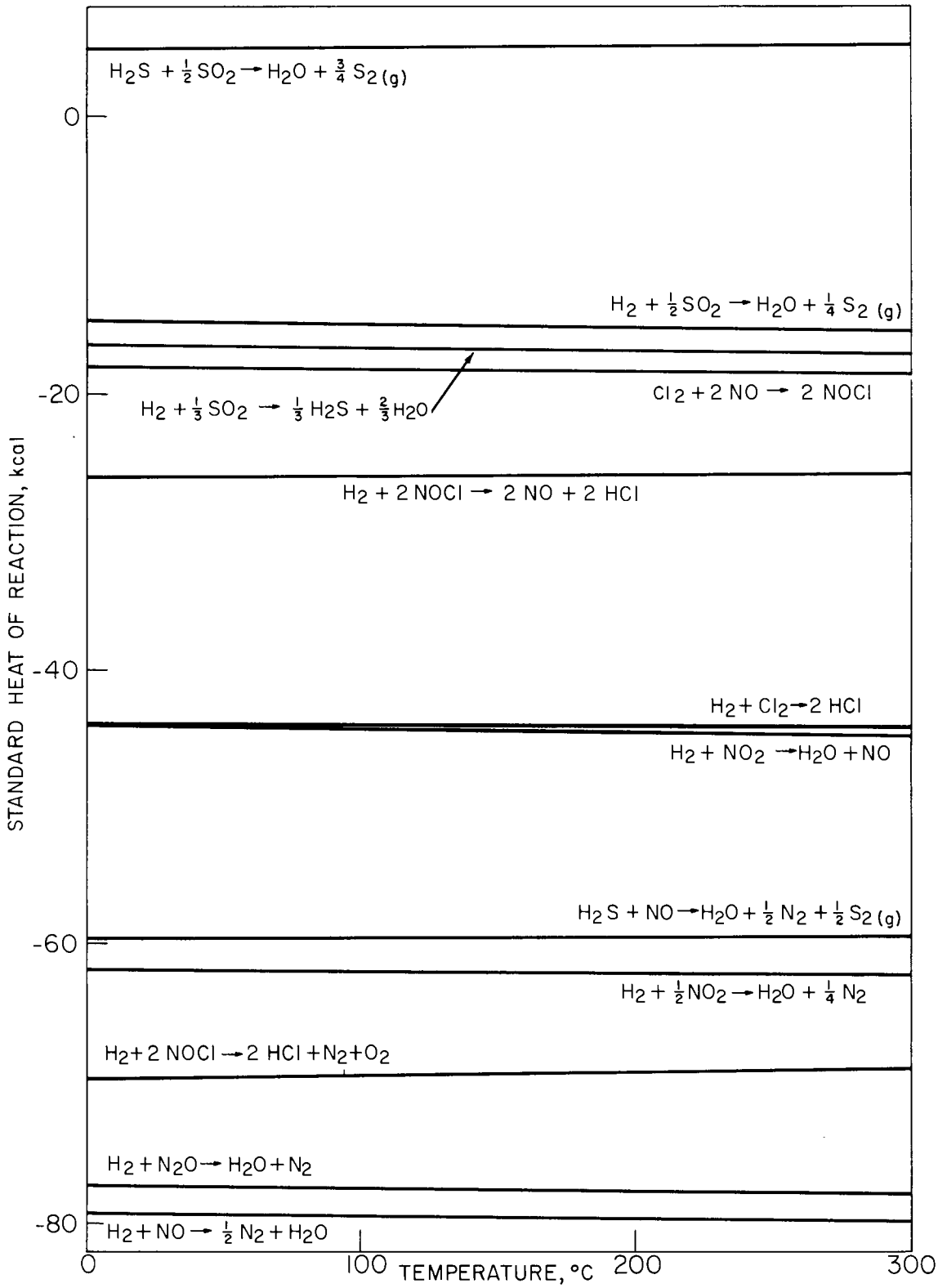

Fig. 1. Heats of reaction vs temperature for twelve gaseous reactions ($\Delta H°$ for reactions as written).

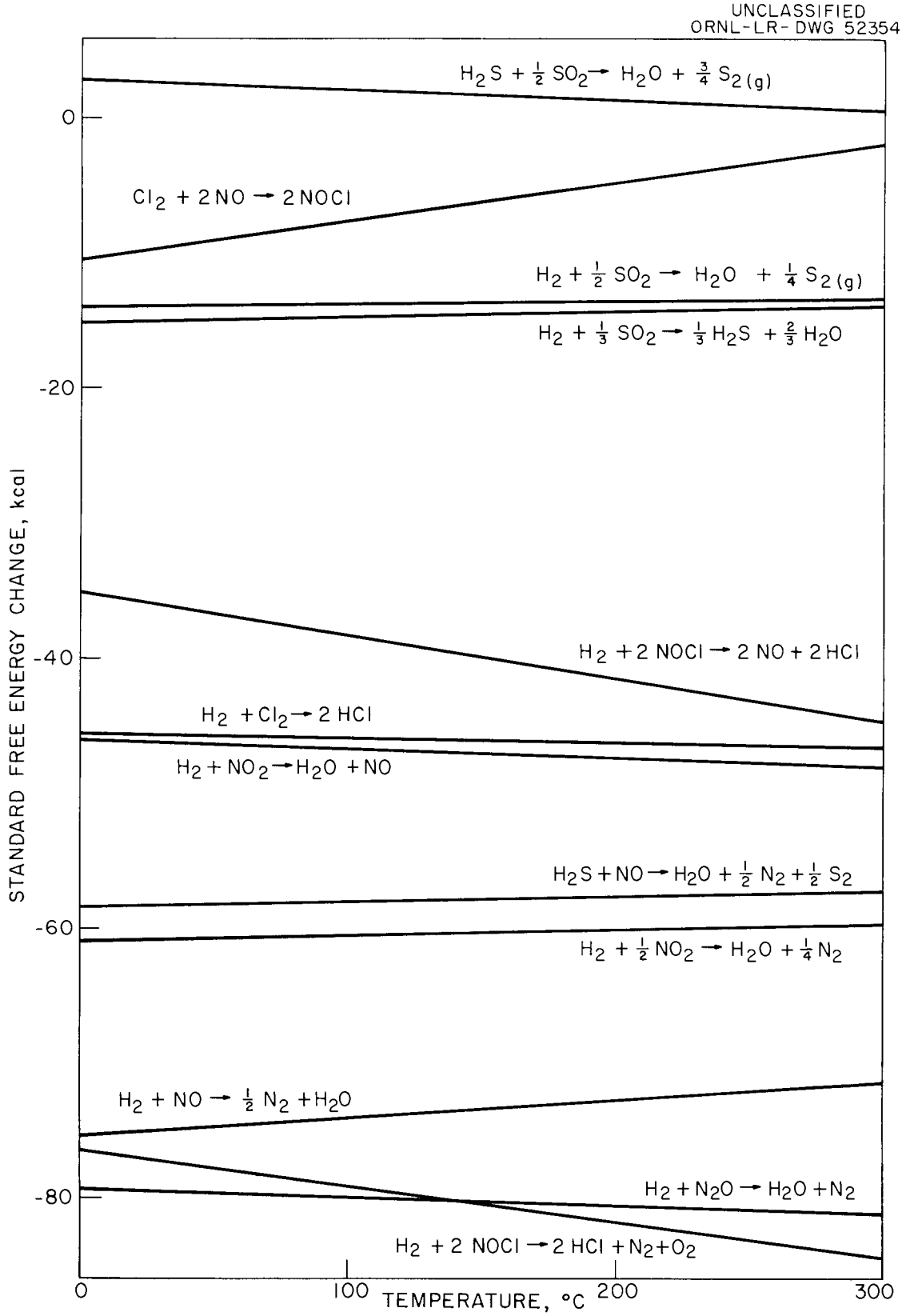

Fig. 2. Free energy changes vs temperature for gaseous reactions as written.

Table 1. Reactions 1-12 Arranged in Decreasing Order of ΔH^o_{373}

Reaction No.	Components of Reaction	ΔH^o_{373}, kcal/g-atom H or equivalent	Slope of ΔH^o_{373} vs Temperature Curve
3	$H_2 + NO$	-39.76	-
1	$H_2 + N_2O$	-38.62	-
2	$H_2 + NOCl$	-34.60	+
4	$H_2 + NO_2$	-30.99	-
12	$H_2S + NO$	-29.82	0
5	$H_2 + NO_2$	-22.19	-
6	$H_2 + Cl_2$	-22.10	-
7	$H_2 + NOCl$	-13.00	+
8	$Cl_2 + NO$	- 9.10	-
10	$H_2 + SO_2$	- 8.32	-
9	$H_2 + SO_2$	- 7.49	-
11	$H_2S + SO_2$	+ 2.48	+

Table 2. Reactions 1-12 Arranged in Decreasing Order of ΔF^o_{373}

Reaction No.	Components of Reaction	ΔF^o_{373}, kcal/g-atom H or equivalent	Slope of ΔF^o vs Temperature Curve	For Balanced Equation	
				Value of ΔS^o_{298}	Change in No. of Moles
1	$H_2 + N_2O$	-39.96	-	+ 7	0
2	$H_2 + NOCl$	-39.62	-	+27	+1
3	$H_2 + NO$	-37.17	+	-27	-1
4	$H_2 + NO_2$	-30.27	+	-14	-1
12	$H_2S + NO$	-29.02	+	- 4	0
5	$H_2 + NO_2$	-23.39	-	+ 7	0
6	$H_2 + Cl_2$	-22.9	-	+ 5	0
7	$H_2 + NOCl$	-19.14	-	+33	+1
10	$H_2 + SO_2$	- 7.38	+	- 8	-1
9	$H_2 + SO_2$	- 7.03	+	-14	-1
8	$Cl_2 + NO$	- 3.80	+	-28	-1
11	$H_2S + SO_2$	+ 1.10	-	+28	+1

The H_2-NO reaction (reaction 3) was the most exothermic in the list, with ΔH^o = -39.76 kcal/g-atom H. In contrast, the H_2S-SO_2 reaction (reaction 11) was slightly endothermic, with ΔH^o = +2.5 kcal/g-atom H. The group of reactions falls into roughly the same order when arranged by ΔF^o values (Table 2). The H_2-N_2O reaction (reaction 1) showed the largest change in free energy, -40.0 kcal/g-atom H, or an equilibrium constant, K, of 2 x 10^{23}.

The slopes of each of the 12 free-energy function curves were tested for conformity to the relation

$$\left(\frac{d\Delta F^o}{dT}\right)_P = \frac{\Delta F^o - \Delta H^o}{T} = -\Delta S^o$$

and no deviations were found at the temperature of chief interest, 373°K. The slope of the ΔF^o vs temperature curves is strongly negative, about -3.5 kcal/100°, for reactions in which the ΔS^o is about 27 cal/deg, and equally strongly positive for reactions in which the $-\Delta S^o$ is ~27 cal/deg. Entropy changes of these amounts are typical for a net change of 1 mole of gas during the overall reaction.

3.0 COMBUSTIBILITY OF VARIOUS GAS MIXTURES

A flame is propagated through a mixture of two or more gases if the ratio of the gases lies within the limits of flammability. Such limits can be determined only by experiment (6). An initially slow-moving combustion wave will accelerate to a detonation wave if the composition of the mixture permits. In general, the velocity of the detonation wave, when established, is constant. The velocity is little influenced by changes in the initial pressure and temperature of the gas mixture, and is independent of the method of initiation, whether by spark, flame, or detonation wave from another source (7). In contrast, the limits of flammability are very much dependent upon the sources of ignition and its intensity, the initial temperature of the gas mixture, and relatively large changes in the initial pressure (5). This survey does not include the special cases of catalytic action effected by substances in dissolved (8) or slurry (9) form.

3.1 <u>For the Reaction</u> $H_2 + N_2O \longrightarrow H_2O + N_2$, the thermodynamic relations are:

$$\Delta H_T^o = -75{,}571 - 3.62\,T + 0.37 \times 10^{-3}\,T^2 - 2 \times 10^5/T$$

$$\Delta F_T^o = -75{,}571 - 32.224\,T + 3.62\,T \ln T - 0.37 \times 10^{-3}\,T^2 - 10^5/T$$

The free energy of formation of nitrous oxide at 25°C is positive (+24.76 kcal); the possibility of explosive decomposition of N_2O is consequently a subject of interest, and comment on this is in order before discussing the H_2-N_2O reaction written above. Volmer and Kummerow (10) state that the thermal decomposition of nitrous oxide proceeds unimolecularly with a heat of activation of 57.5 kcal/mole. This has been discussed polemically (11), but later confirmed (12) (53 kcal/mole). Zeldovich and Jakovlev (13) found that at sufficiently high temperatures (above 1100°C) a thermal explosion of nitrous oxide occurred through self-ignition in

quartz, accompanied by a blue flame and a pressure rise. According to Melville (14) who studied the N_2O-H_2 reaction at 550-700°C, the rate of reaction between the two gases was faster than the rate of decomposition of N_2O. It thus appears that the latter is of no consequence at temperatures of 100-200°C except in situations where sensitization by ammonia is possible. Jones and Kerr (15) noted that the exothermic decomposition of nitrous oxide was apparently catalyzed by small amounts of ammonia when ignition was effected by a spark. Glass tubes containing the mixture at room temperature have been shattered at NH_3/N_2O ratios much below the limit for normal flame propagation, and raising the temperature to 150-250°C had little effect other than slightly widening the limits of the explosive range. Without ammonia, nitrous oxide decomposes very slowly into nitrogen and oxygen below 700°C (16). Hunter found (17) that he could conveniently measure the velocity of this reaction at 600-850°C. In the absence of ammonia, then, the reaction $2N_2O \longrightarrow 2N_2 + O_2$ may be neglected.

Mixtures of hydrogen and nitrous oxide have been initiated to combustion or detonation by at least three means:

(a) Heating the mixture: The lowest recorded temperature (18) was 484°C, at which explosion occurred after 5 sec under a total pressure of 150 mm Hg. At a total pressure of 760 mm Hg the "5-sec ignition temperature" was raised to 543°C.

(b) Ignition with an electric spark: Dixon (19) observed a rate of detonation of 2305 meters/sec at normal atmospheric pressure. At total pressures of 500, 760, and 1000 mm Hg the observed rates were 2094, 2307, and 2302 meters/sec, respectively. These measurements were conducted in a lead tube 100 meters long, and 9 mm dia, wound on a drum 2 ft dia. The wall thickness was not specified, but apparently rupture by explosion did not occur. During its passage down the lead tube, the detonation wave broke fine wire "bridges," which served as electrical impulses on the time scale for the velocity measurements. A finite length of tube ahead of the bridges provided an opportunity for the wave to attain its ultimate constant rate of speed. For atmospheric pressure measurements a span of only 4 ft was used for complete acceleration; for lower pressures 20 ft was interposed between the firing point (point of ignition) and the first bridge.

(c) Initiation with a detonator: When a lead styphnate—lead azide—tetryl detonator was used to initiate the H_2-N_2O mixture at room temperature, a detonation rate of 2200 to 2590 meters/sec was observed (20). By way of comparison, a H_2-O_2 mixture produced a rate of 2780 to 2820 meters/sec. These experiments were conducted in glass tubes 1.3 cm i.d. and 1.5 meters long. In the case of detonation-induced reactions, the initial speed exceeded the "normal speed" for a period of ~0.25 msec, corresponding to a run of ~50 cm before slowing down to its constant speed.

The propagation of a flame in hydrogen—nitrous oxide mixtures has also been studied by van der Wal (21) and Posthumus (22). These Dutch experimenters found that with about 23% or more N_2O the binary mixture gave a violent explosion upon ignition by spark between platinum electrodes. At about 5% N_2O a yellow flame glided through the mixture without noise. Measurements were made at room temperature and atmospheric pressure. Van der Wal (21) stated that an excess

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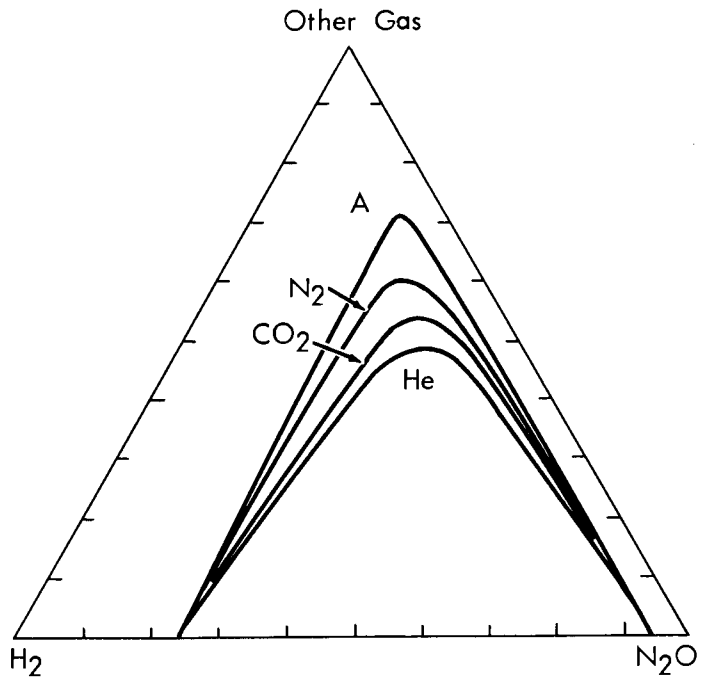

Fig. 3. Effect on flammability of adding helium, carbon dioxide, nitrogen and argon to an H_2-N_2O mixture (Posthumus[22]).

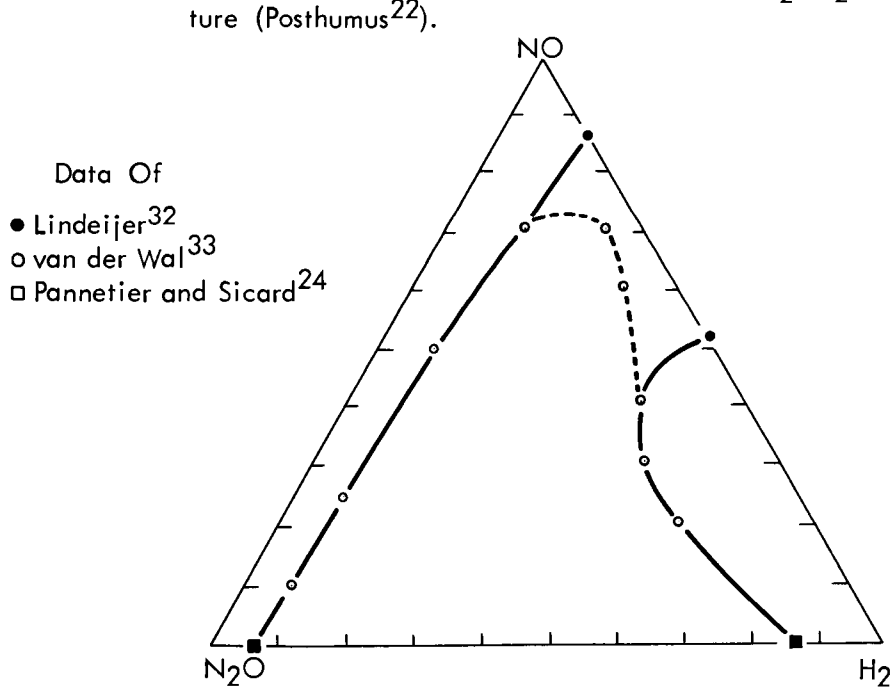

Fig. 4. Effect on flammability of adding nitric oxide to an H_2-N_2O mixture.

of N_2O produced a brown color when exploded; with an excess of hydrogen (or other gases tested) a brown color did not result, but instead considerable water was formed.

The lower limit was redetermined by Smith and Linnett (23) with a more powerful spark, 2 μf of capacitance at 4000 volts, yielding a new N_2O limit of 16.19%. These workers used a tube 5 cm dia, whereas Posthumus used a 1.6-cm-dia tube. More recently two French investigators obtained limits of 14 and 94.2% N_2O, respectively (24), and gave limits for subatmospheric pressures.

A peculiar behavior of nitrous oxide was noted by Danby and Hinshelwood (25). If N_2O is added to an H_2-O_2 mixture at 550°C it behaves as an inert gas, but if oxygen is added last to a N_2O-H_2 mixture immediate ignition occurs. The cause may be a trace of NO produced, because minute amounts of NO are known to cause immediate ignition.

Posthumus (22) also studied the effect of adding inert gases to the binary mixture and determined the explosion limits of the resulting ternary mixtures. In a plot of his data (Fig. 3) the top of each of the four curves essentially represents the maximum amount of inert gas that may be present in a mixture of H_2 and N_2O that still retains a degree of combustibility. The difference in heat capacities of equal volumes of helium and argon may be responsible for the difference in effect as shown in the graph and the table below:

"Inert" gas	Limiting amount, %
Helium	50
Carbon Dioxide	54
Nitrogen	60.8
Argon	71.6

This same order of the four inert gases occurs again with respect to their effect on the original limits of hydrogen and nitrous oxide. Helium is most effective in narrowing the limits of the combustible mixture, while at the other extreme, argon widens the limits slightly (Fig. 3).

3.2 For the Reaction $H_2 + 2NOCl \longrightarrow 2HCl + N_2 + O_2$ the thermodynamic relations are:

$$\Delta H_T^o = -67{,}701 - 1.48\ T - 0.12 \times 10^{-3}\ T^2 - 3.32 \times 10^5/T$$

$$\Delta F_T^o = -67{,}701 - 38.657\ T - 1.48\ T \ln T + 0.12 \times 10^{-3}\ T^2 - 1.66 \times 10^5/T$$

The thermochemical data indicate that the above reaction is nearly as exothermic as the hydrogen-nitrous oxide reaction discussed in Sect. 3.1. According to Davy (26) nitrosyl chloride explodes if mixed with an equal amount of hydrogen. Although NOCl could be present in the vapor phase by entrainment or by reaction of nitrogen oxides with chlorine (Sect. 3.8) or HCl, the likelihood of appreciable concentrations accumulating above a dissolvent mixture is very low for reasons of hydrolysis (27). NOCl is readily hydrolyzed by contact with water at or above

room temperature (28). It is of interest that NOCl may act as a sensitizer for certain reactions; e.g., it was found (29) that small amounts of NOCl decrease the ignition temperature of $2H_2 + O_2$ mixtures more than 200°C.

3.3 For the reaction $2H_2 + 2NO \longrightarrow 2H_2O + N_2$ the thermodynamic relations are:

$$\Delta H_T^o = -155{,}315 - 8.84\ T + 2.227 \times 10^{-3}\ T^2 - 3.126 \times 10^5/T$$

$$\Delta F_T^o = -155{,}315 - 32.536\ T + 8.84\ T \ln T - 2.227 \times 10^{-3}\ T^2 - 1.563 \times 10^5/T$$

Although nitric oxide has a free energy of formation of +20.719 kcal/mole, it is apparently fairly stable; according to Guye and Schneider (30) NO is decomposed at atmospheric pressure by heat only at temperatures above 575°C maintained for several hours, even in the presence of catalytic agents such as platinized asbestos.

Nitric oxide has been reduced to nitrogen at 826°C, and the reaction has been established (31) as termolecular with a heat of activation of 44 kcal/mole. The experimentally determined order of reaction is slightly less than 3.0, since a small amount of surface reaction is nearly independent of the pressure of hydrogen (31). The reaction proceeds in accordance with the equation

$$\frac{-d[NO]}{dt} = k\ [NO]^2\ [H_2]$$

and the experimentally determined value of $k = 1.24 \times 10^{-7}\ mm^2/sec$.

Lindeijer (32) observed the propagation of a flame through a mixture of hydrogen and nitric oxide. His flammability limits were 13.5 and 49.4% hydrogen, respectively. Light and a contraction accompanied the reaction, but the latter appeared to be complicated since the products included some NO_2 in addition to water.

The ternary system hydrogen—nitrous oxide—nitric oxide was studied (33), and the region of flammability was plotted on a triangular diagram (Fig. 4). The spark used was too weak to ignite any mixture of hydrogen and nitric oxide alone. Three years later Lindeijer (32) established definite explosion limits for H_2-NO mixtures (discussed in the preceding paragraph). These data were combined with the earlier data to provide a more realistic diagram; the solid lines in Fig. 4 show the more probable boundaries of the flammable area.

3.4 For the reaction $4H_2 + 2NO_2 \longrightarrow 4H_2O + N_2$ the thermodyanmic relations are:

-61,800 cal/mol H_2

$$\Delta H_T^o = -243{,}167 - 11.26\ T + 2.03 \times 10^{-3}\ T^2 - 3.06 \times 10^5/T$$

$$\Delta F_T^o = -243{,}167 - 62.362\ T + 11.26\ T \ln T - 2.03 \times 10^{-3}\ T^2 - 1.53 \times 10^5/T$$

For a discussion see the next paragraph.

3.5 For the reaction $H_2 + NO_2 \longrightarrow H_2O + NO$ the thermodynamic relations are:

$$\Delta H_T^o = -43{,}069 - 2.58\ T + 0.33 \times 10^{-3}\ T^2 - 1.43 \times 10^5/T$$

$$\Delta F_T^o = -43{,}069 - 24.668\ T + 2.58\ T \ln T - 0.33 \times 10^{-3}\ T^2 - 0.71 \times 10^5/T$$

Pierce and Noyes (34) reported that a mixture of nitrogen dioxide and hydrogen reacted explosively when subjected to a discharge (presumably an electric discharge was meant), but that activation of the nitrogen dioxide by light alone will not cause reaction. Information appears to be lacking concerning explosion limits of this binary mixture.

Guye and Schneider (30) carried the reduction of nitrogen dioxide completely to ammonia in the presence of catalysts such as platinized asbestos, with a conversion of 77% at 280°C. With asbestos containing rhodium, an H_2-NO mixture produced NH_3 and H_2O at temperatures as low as 250°C (35).

3.6 For the reaction $H_2 + Cl_2 \longrightarrow 2HCl$ the thermodynamic relations are:

$$\Delta H_T^o = -43{,}031 - 2.66\ T + 0.68 \times 10^{-3}\ T^2 - 1.08 \times 10^5/T$$

$$\Delta F_T^o = -43{,}031 - 22.760\ T + 2.66\ T \ln T - 0.68 \times 10^{-3}\ T^2 - 0.54 \times 10^5/T$$

This well-known light-activated reaction is stated (36) to proceed without light at 250°C. Rates of detonation at 14°C in H_2-Cl_2 mixtures were observed by Dixon (37) to be 1745 m/sec (dry) and 1720 (moist). These were initiated by the shock wave from an H_2-O_2 filled tube which was joined directly to the H_2-Cl_2 tube.

Flammability limits were determined by Weissweiler (38) for both dry and moist binary mixtures as follows:

Dry Gases

Lower limits of flammability:

Down to 3.5% H_2 + 96.5% Cl_2	Thrust, no flame
7.0% H_2 + 93% Cl_2	Thrust with flame, no detonation
17.5% H_2 + 82.5% Cl_2	Detonation with flame

Upper limits of flammability:

Up to 77% H_2 + 23% Cl_2	Detonation with flame
83% H_2 + 17% Cl_2	Detonation, no flame
97% H_2 + 3% Cl_2	Thrust, no flame

Moist Gases

Lower limits of flammability:

Down to 4% H_2 + 96% Cl_2	Thrust, no flame
7% H_2 + 93% Cl_2	Thrust with flame, no detonation
24% H_2 + 76% Cl_2	Detonation with flame

Upper limits of flammability:

Up to 76.5% H_2 + 23.5% Cl_2	Detonation with flame
80.5% H_2 + 19.5% Cl_2	Detonation, no flame
97% H_2 + 3% Cl_2	Thrust, no flame

Other workers (32, 39) have also determined flammability limits for the binary mixture of hydrogen and chlorine and then determined the effect of adding a third component—nitrogen, nitric oxide, or hydrogen chloride. The results of this work are outlined below.

Lindeijer's limits of flammability (32) were:

10% H_2 + 90% Cl_2
84% H_2 + 16% Cl_2

and the admixture with nitrogen gas yielded results which are plotted in Fig. 5. Nearly 70% nitrogen was required to make the two explosion limits of hydrogen and chlorine coincide. The same author remarks that "the flame [of H_2-Cl_2] is difficult to see, even in the dark."

The ternary mixture hydrogen—chlorine—nitric oxide was investigated by Lindeijer (32). The results are shown in Fig. 6. He also observed the effect on the ternary of the presence of 10% nitrogen (Fig. 7); the two explosive regions which formerly overlapped in the ternary diagram were withdrawn from each other and rendered quite distinct by the nitrogen diluent.

The objective of two Russian workers (39) was the study of the effect of adding as the third component the product of the reaction, hydrogen chloride gas. For the binary mixture of H_2 and Cl_2 they observed

Lower limit: 5.5% hydrogen
Upper limit: 86% hydrogen

There was no explosion above 70% HCl, and the explosive range was not materially changed by the third component (Fig. 8). To the ternary, consisting of H_2, Cl_2, and HCl, a fourth component (CO_2, N_2, and O_2, respectively) was added and the effect on the combustion limit was determined (39). Details of this work are not given here.

3.7 For the reaction $H_2 + 2NOCl \longrightarrow 2NO + 2HCl$ the thermodynamic relations are:

$$\Delta H_T^o = -24{,}523 - 1.24\ T - 0.21 \times 10^{-3}\ T^2 - 3.44 \times 10^5/T$$

$$\Delta F_T^o = -24{,}523 - 43.151\ T + 1.24\ T \ln T + 0.21 \times 10^{-3}\ T^2 - 1.72 \times 10^5/T$$

A discussion of the above binary mixture is found in Sect. 3.2.

3.8 For the reaction $Cl_2 + 2NO \longrightarrow 2NOCl$ the thermodynamic relations are:

$$\Delta H_T^o = -18{,}507 - 1.42\ T + 0.89 \times 10^{-3}\ T^2 + 2.36 \times 10^5/T$$

$$\Delta F_T^o = -18{,}507 + 20.321\ T + 1.42\ T \ln T - 0.89 \times 10^{-3}\ T^2 + 1.180 \times 10^5/T$$

which are in good agreement with the experimental data of Beeson and Yost (40), who studied the equilibrium over the temperature range 100-220°C. The reaction between chlorine and nitric oxide is apparently not a rapid one since these investigators allowed several hours at these temperatures to reach equilibrium. At 15°C the velocity constant was determined (41) to be 5.7×10^{-6} (mm Hg, time in minutes) at a total pressure of 1 atm. Stoddart (42) obtained values of 2×10^{-7} at 15°C and 4.5×10^{-7} at 25°C at a total pressure of about 2/3 atm.

The reaction between chlorine and nitric oxide can be detected down to -180°C, and it has been reported (43) that this reaction gives rise to $NOCl_2$ as well as NOCl.

3.9 For the reaction $4H_2 + 2SO_2 \longrightarrow 4H_2O + S_2$ (g) the thermodynamic relations are:

$$\Delta H_T^o = -56{,}013 - 9.62\ T + 1.16 \times 10^{-3}\ T^2 - 1.89 \times 10^5/T$$

$$\Delta F_T^o = -56{,}013 - 56.369\ T + 9.62\ T \ln T - 1.16 \times 10^{-3}\ T^2 - 0.945 \times 10^5/T$$

A thermodynamic study was previously made by Lepsoe (44) using older fundamental data, but agreement with the above is good. Since that time an experimental study has been conducted (45) with an iron sulfide—alumina catalyst for the purpose of determining the feasibility of sulfur recovery from petroleum waste gases containing sulfur dioxide. The process was fairly effective at 315°C, but it was found impossible to reduce SO_2 with H_2 directly to elemental sulfur without simultaneous formation of H_2S.

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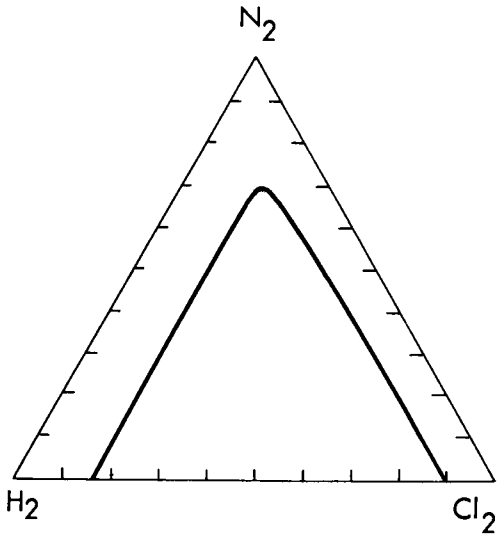

Fig. 5. Effect on flammability of adding N_2 to an H_2-Cl_2 mixture (Lindeijer[32]).

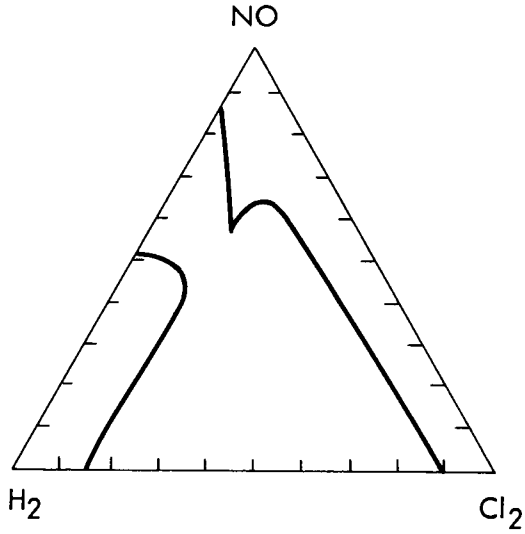

Fig. 6. Effect on flammability of adding NO to an H_2-Cl_2 mixture (Lindeijer[32]).

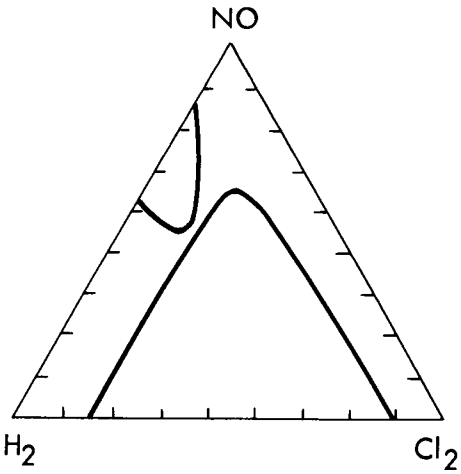

Fig. 7. Separate explosion regions in the H_2-Cl_2-NO system when 10% N_2 is present (Lindeijer[32]).

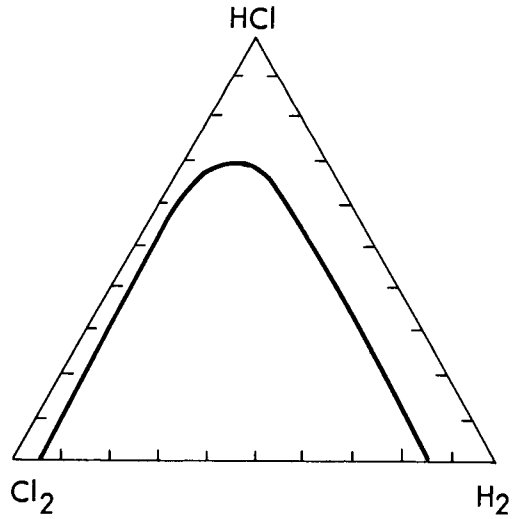

Fig. 8. Effect on flammability of adding HCl to H_2-Cl_2 mixtures (Kunin and Serdyukov[39]).

The free energy of reaction, only -14.2 kcal/mole H_2 at room temperature, decreases slightly with increase in temperature (Fig. 2). Doumani and co-workers (45) state that below 325°C the reduction of SO_2 with H_2 (in the presence of 92.5% N_2 diluent) was not detectable; at 370°C the reaction proceeded slowly, and at 425 to 480°C, quite rapidly. Thus this reaction is definitely a high-temperature process which would not be involved at ordinary fuel processing temperatures. It is of interest to note, however, that the equilibrium in the conversion to water and elemental sulfur was studied by Randall and co-workers (46, 47), who showed that the reaction is indeed reversible, the reverse reaction being very rapid at the melting point of sulfur.

3.10 For the reaction $3H_2 + SO_2 \longrightarrow 2H_2O + H_2S$ the thermodynamic relations are:

$$\Delta H^o_T = -46{,}660 - 8.58\ T + 1.98 \times 10^{-3}\ T^2 - 1.22 \times 10^5/T$$

$$\Delta F^o_T = -46{,}660 - 43.302\ T + 8.58\ T \ln T - 1.98 \times 10^{-3}\ T^2 - 0.61 \times 10^5/T$$

Near the temperature range of interest (100°C) the free energy change for this reaction is about -14.8 kcal/mole H_2, which is thus equally as favorable for the production of water and hydrogen sulfide as for the production of water and sulfur (reaction 9; see Sect. 3.9) where $\Delta F^o_{373} = 14.1$ kcal/mole H_2. Indeed, Doumani and co-workers (45) could not eliminate hydrogen sulfide as an unwanted by-product in their experimental study of the catalytic reduction of sulfur dioxide. Without catalysts no reaction was obtained at 280°C, but the presence of Ni_3S_2 gave rise to 20% conversion to H_2S at 160°C and 80% conversion at 225°C (48). Strong light at room temperature produced no reaction between hydrogen and sulfur dioxide (48).

3.11 For the reaction $4H_2S + 2SO_2 \longrightarrow 4H_2O + 3S_2$ (g) the thermodynamic relations are:

$$\Delta H^o_T = +18{,}587 + 5.48\ T - 4.36 \times 10^{-3}\ T^2 - 0.79 \times 10^5/T$$

$$\Delta F^o_T = +18{,}587 + 4.8162\ T - 5.48\ T \ln T + 4.36 \times 10^{-3}\ T^2 - 3.95 \times 10^4/T$$

The free energy of reaction, only -2.8 kcal/mole H_2S at room temperature, decreases numerically with increase in temperature, reaching zero at a temperature of about 460°C (Fig. 2). This reaction is the basis for a commercial process (49) which was designed to "sweeten" sour petroleum gases, and operates at 232°C with a catalyst. Doumani and others (45) found that alumina was an effective catalyst at 210°C and atmospheric pressure, obtaining "complete conversion" to water and sulfur. These considerations lead to the conclusion that the H_2S-SO_2 reaction need not be considered under the conditions existing in dissolvent operations.

3.12 For the reaction $2H_2S + 2NO \longrightarrow 2H_2O + N_2 + S_2$ (g) the thermodynamic relations are:

$$\Delta H^o_T = -119{,}732 + 1.44\ T - 1.390 \times 10^{-3}\ T^2 + 0.36 \times 10^5/T$$

$$\Delta F^o_T = -119{,}732 - 17.608\ T - 1.44\ T \ln T + 1.39 \times 10^{-3}\ T^2 + 18{,}000/T$$

The heat of reaction at room temperature lies rather close to that for the reaction $2H_2 + O_2 \longrightarrow 2H_2O$ (-29.82 as compared to 28.90 kcal/mole, computed on a single atomic weight of hydrogen and assuming all reactants and products are gaseous). The limits of flammability of the two reactions are quite different, however, illustrating the unpredictability of such limits. Van der Wal (21) found the H_2S concentration limits to be 20 and 55% for the reaction with nitric oxide, while the H_2 concentration limits have been recorded (6) as 3.9 and 95.8% for the reaction with O_2. Van der Wal described the reaction as one in which a blue flame was propagated without perceptible sound, forming much water and elemental sulfur. In view of this there is evidently little or no tendency for NO to oxidize H_2S to SO_2, i.e., beyond the stage represented by eq. 12. Accordingly, attention has not been given to a thermodynamic treatment of the equation

$$2H_2S + 6NO \longrightarrow 2H_2O + 3N_2 + 2SO_2.$$

4.0 GENERAL DISCUSSION

Of the 12 reactions (Sect. 2.0), Nos. 1-7 and 12 are capable of conducting a combustion wave, and with one exception (reaction 12, the H_2S-NO reaction), the combustion wave readily accelerates to detonation velocities. Reactions 1-7 and 12 would arise only in Darex processing and, as expected, are the most exothermic, having heats of reaction in the range -13 to -40 kcal/mole (Table 1). Mixtures which are known to detonate all include hydrogen gas as one of the participants, with a nitrogen oxide, NOCl, or Cl_2 as the other participant. Hydrogen gas with oxides of nitrogen and/or chloride accordingly represent the potentially most dangerous gaseous mixtures of those apt to be generated by fuel element dissolution.

For the remaining four binary mixtures (reactions 8-11) either the reduction of SO_2 or the formation of NOCl is involved. The heats of reaction range from -9 to +2.5 kcal (Table 1), and propagation of a flame appears to be impossible at atmospheric pressure. Therefore no explosion hazard is involved in use of the Sulfex process where conditions for such reactions might occur.

5.0 THERMODYNAMIC DATA AND TREATMENT

The sources of thermochemical and thermodynamic data were the several governmental compilations now available (50-52). Conventional methods (53) were used in deriving the ΔH^o and ΔF^o equations as functions of temperature.

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