INVESTIGATION OF THE CHEMICAL KINETICS OF AN ADVANCED HIGH ENERGY PROPELLANT SYSTEM

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Introduction

Under Contract NASR-183, New York University is investigating the kinetics of systems related to the OF_2/B_2H_6 propellant. Among these are the kinetics of the thermal decomposition of OF_2, F_2, and B_2H_6, respectively, and the kinetics of the reaction between hydrogen and fluorine. Another program is commencing, in which the kinetics of the low temperature solid phase kinetics of the reaction between hydrazine and nitrogen tetroxide is to be investigated. This latter system is of interest because of reported engine difficulties in space.

1. Chemistry of "Restart Pressure Spikes" in the N_2H_4/N_2O_4 Engine

The following hypothesis regarding the origin of "restart pressure spikes" in the engine is being used as the model for the laboratory studies: At the end of a combustion cycle, N_2O_4 vaporizes before the fuel line is cleared of N_2H_4. N_2H_4 expands into the low pressure combustion chamber, is cooled, and condenses on the chamber wall. At the beginning of the next cycle, N_2O_4 flows into the chamber before N_2H_4, and, also, expands and then condenses on the chamber wall. When N_2H_4 enters the chamber, N_2O_4 reacts rather than condenses. The duration and intensity of combustion is too low to heat the chamber walls sufficiently to vaporize the condensates. The effect of the combustion on the condensates is that the attendant radiation causes photolytic reactions. At the end of the combustion cycle, N_2H_4 again condenses. The process continues until chemical species are formed which can be initiated into explosive decomposition by radiation from the combustion reaction.

Experimentally, this model is being pursued in the following way to elucidate the chemistry during this sequence and also the thermochemical phenomenon:

The sequence of N_2H_4 deposition, N_2O_4 deposition, and photolysis is being studied in a cell in which reactants and products, in the condensed phase or the gas phase, can be analyzed by a rapid-scanning IR-UV-Visible spectrometer. The spectrometer is the Warner-Swasey 501 which is capable of a maximum scan speed of 0.001 second over portions of the spectra. The overall set up is shown in Figure 1. The cell is placed in the path of a spectrometer radiation source, used for obtaining absorption spectra, or in the path of an arc image furnace, which is used as a source of photolytic radiation. In the set up as shown, spectra of the condensates on the cooled cell window are obtainable. For obtaining the gas phase spectra, in addition, another cell is used which is in the form of a cross so that windows can be placed at right angles to the ones being used to study the condensates. By rotating the cell, the gas phase can be analyzed. A blow-up of the cell is shown in Figure 2. First, the cell is evacuated through the stopcock, then the cell window is cooled with nitrogen, N_2H_4 is condensed, and then the "break seal" tube which contains liquified N_2O_4 is rotated thereby breaking the seal and releasing drops of N_2O_4

2. OF_2/B_2H_6 Engine

The question of interest in this study is whether or not the diborane/oxygen difluoride engine will conceivably display pressure spiking phenomena similar to that in the N_2H_4/N_2O_4 engine operating in space conditions. The model assumed for the formation of explosive compounds was analogous to the one used in the N_2H_4/N_2O_4 engine. Tersely, the fuel condenses in the combustion chamber at the end of the combustion cycle; the oxidizer condenses at the beginning of the next cycle, and the condensate is subject to photolysis.

For the initial investigation, the approach was to condense the oxidizer and fuel on a cold surface adjacent to the pinhole leak of a rapid scanning mass spectrometer and to analyze the volatiles at the surface warmed up. This set up has been described previously when it was used in the N_2H_4/N_2O_4 study. For this study, diborane was first condensed on the cold surface at liquid nitrogen temperature. However, it was not possible to condense OF_2 at 100 mm pressure, the maximum pressure that it is feasible to handle OF_2 in our system. However, an observation of prime importance was made on evaporating the condensed diborane. The least volatile compounds were boron hydride polymers. On further investigation, it was found that such polymers form when cylinders of diborane are stored at room temperature. Polymer

formation is retarded when the cylinders are stored in a freezer. On the other hand, the fact that polymers are not present initially does not preclude the formation and deposition of polymers in the combustion chamber. In fact, it is most probable because, on shutdown, the temperature in the combustion chamber needs to be only about 100°C to bring about pyrolysis and polymerization of diborane. The importance of these polymers is that, in addition to their relatively low volatility, some of these polymers are reactive. Therefore, it is our conclusion, that the investigation of the OF_2/B_2H_6 should center upon these problems:

1. Can stable polymers become unstable when subjected to photolysis?

2. The nature of the interaction between these polymers and OF_2.

3. An analysis of the combustion chamber wall deposits in engines after shutdown to determine the nature of the polymers formed.

3. The Effect of Oxygen on the Hydrogen/Fluorine Reaction

The effect of oxygen on reaction of hydrogen and fluorine, diluted with helium, was studied in a flow reactor coupled to a mass spectrometer. The ratios of the reactant concentrations, temperatures, reaction times, and pressures were varied. The data are presented in Tables 1 - 3. In these Tables, the amount of fluorine unreacted in the presence of oxygen is compared to the amount of fluorine unreacted in the absence of oxygen. The data in the columns designated D refer to the conditions when oxygen is absent. These runs were made at different times, rather than consecutively, and, therefore give a measure of the precision and comparability of the data. The significance of the data is, at present, still under consideration, therefore, this data will not be discussed in this report.

Future Work

We will be continuing our work in the simulated "cell-engine". After a study of the pure oxidizer and pure fuel (N_2H_4 and UMDH) reactions, the effect of additives, especially urea, which in "test tube" studies inhibited the formation of azides when UMDH was the fuel, will be investigated.

The next step in the B_6H_6/OF_2 engine study will be a thorough literature survey of the properties of boron hydride polymers which have been the subject of intensive investigation during the past ten years.

The data from our study of the effect of oxygen on the reaction between hydrogen and fluorine will be analyzed with special emphasis on its significance with respect to a similar study performed at Atlantic Research under different conditions.

Explanation of the following Tables on the Effect of Oxygen on the Reaction Between Hydrogen and Fluorine

I. Compositions of Mixtures Designated by Letters in the Tables

A = 0.5% O_2, 4% F_2, 50% H_2, 45.5% He

B = 1.5% O_2, 4% F_2, 50% H_2, 44.5% He

C = 3.0% O_2, 4% F_2, 50% H_2, 43.0% He

D = 4% F_2, 50% H_2, 46% He

II. Values listed in column under the Composition Designations refer to the concentration of unreacted fluorine in units of moles/liter x 10^{-6}.

Table 1. Effect of Oxygen at a Total Reactor Pressure of 25 Torr.

Temp.(°C)	Time (sec.)	A	B	C	D	D
600	0	18.44	18.44	18.44	18.44	18.44
	.0005	2.21	2.58	2.76	7.37	9.95
	.001	0.18	0.18	0	6.08	6.63
	.002	0	0	0	4.05	3.87
	.003	0	0	0	1.29	2.95
	.004	0	0	0	0	2.21
	.005	0	0	0	0	1.47
	.007	0	0	0	0	0.55
	.010	0	0	0	0	0
550	0	19.56	19.56	19.56	19.56	19.56
	.0005	2.73	3.71	3.13	10.95	13.49
	.001	0.39	0.39	0.58	8.02	10.75
	.002	0	0	0	4.49	7.04
	.003	0	0	0	5.28	5.67
	.004	0	0	0	4.10	4.69
	.005	0	0	0	3.32	3.71
	.007	0	0	0	1.95	2.54
	.010	0	0	0	0.78	1.56
	.015	0	0	0	0	0.58

c.

Table #1 (continued)

Temp.(°C)	Time (sec.)	A	B	C	D	D
500	0	20.82			20.82	20.82
	.0005	13.32			17.49	18.12
	.001	12.28			15.41	15.20
	.002	9.37			11.66	10.41
	.003	7.70			9.78	10.20
	.004	6.45			8.12	8.74
	.005	5.20			7.28	7.70
	.007	3.54			5.41	6.04
	.010	2.08			3.74	4.58
	.015	0			1.87	2.70
450	0	22.26	22.26	22.26	22.26	22.26
	.0005	16.20	18.92	14.47	21.37	21.60
	.001	15.50	18.03	13.36	19.81	19.59
	.002	14.20	14.90	12.47	17.14	16.70
	.003	12.60	12.91	8.90	15.36	15.14
	.004	11.30	11.57	8.01	13.36	13.80
	.005	10.40	10.24	7.79	11.80	13.13
	.007	8.00	7.79	5.56	10.46	10.91
	.010	6.20	5.78	4.00	8.01	9.12
	.015	3.70	3.11	2.00	5.56	6.90

Table #1. (continued)

Temp.(°C)	Time (sec.)	A	B	C	D	D
400	0	23.92	23.92	23.92	23.92	23.92
	.0005	21.20	22.72	22.24	23.92	23.80
	.001	20.80	21.29	22.72	23.92	23.20
	.002	19.80	19.85	19.61	22.48	21.29
	.003	19.10	19.13	16.98	20.57	20.33
	.004	18.10	17.94	16.50	19.37	19.13
	.005	16.90	16.74	16.02	18.89	18.65
	.007	15.50	15.07	14.11	17.70	17.22
	.010	14.10	12.91	12.43	15.54	15.31
	.015	11.90	10.04	10.04	13.63	13.15

Table 2. Effect of Oxygen at a Total Reactor Pressure of 50 Torr

Temp.(°C)	Time (sec.)	A	B	C	D	D	D
600	0	36.88	36.88	36.88	36.88	36.88	36.88
	.001	2.21	4.05	4.05	2.95	3.31	1.47
	.002	0	0	0	0	0	0
	.003	0	0	0	0	0	0
500	0	41.65	41.65	41.65	41.65	41.65	41.65
	.001	9.58	15.41	10.83	16.66	17.49	17.07
	.002	1.66	1.66	1.24	4.99	4.16	4.99
	.003	3.33	2.91	0	4.16	4.04	4.58
	.004	2.08	0	0	2.91	3.74	3.74
	.005	0	0	0	2.49	3.33	3.33
	.007	0	0	0	1.66	2.49	2.49
	.010	0	0	0	0.41	2.08	1.66
	.015	0	0	0	0	0.83	0

Table #2 (continued)

Temp.(°C)	Time (sec.)	A	B	C	D	D	D
450	0	44.53	44.53	44.53	44.53	44.53	44.53
	.001	20.48	27.16	22.71	30.73	32.51	31.17
	.002	14.09	16.14	12.91	13.36	12.02	14.25
	.003	9.79	10.68	10.24	11.13	9.35	10.68
	.004	7.51	8.90	8.01	9.35	8.90	9.35
	.005	7.12	7.57	7.12	8.46	8.46	9.12
	.007	5.34	5.34	5.34	7.12	6.68	7.12
	.010	4.00	4.00	4.00	5.34	5.78	6.23
	.015	1.33	1.33	1.33	3.11	4.45	4.89
400	0	47.84	47.84	47.84	47.84	47.84	47.84
	.001	44.97	40.66	41.14	43.06	41.62	39.71
	.002	33.49	30.14	32.05	31.51	29.18	31.09
	.003	25.35	23.92	25.35	24.87	23.44	25.35
	.004	21.53	20.57	21.53	21.53	21.05	22.48
	.005	19.61	19.13	19.61	19.61	19.13	20.57
	.007	17.22	16.26	16.74	17.22	16.74	18.18
	.010	14.35	13.39	13.87	15.31	14.35	15.78
	.015	11.00	9.56	10.52	11.96	11.96	13.39

Table 3. Effect of Oxygen at a Total Reactor Pressure of 75 Torr.

Temp.(°C)	Time (sec.)	A	B	C	D
600	0	0	55.32	0	0
	.002	0	0.55	0	0
	.003	0	0	0	0
500	0			62.48	0
	.002			2.49	0
	.003			0	0
450	0	66.80	66.80	0	0
	.002	2.000	2.67	0	0
	.003	1.33	1.33	0	0
	.004	.66	.66	0	0
	.005	0	0	0	0

Table#3 (continued)

Temp.(°C)	Time (sec.)	A	B	C	D	D
400	0	71.76	71.76	71.76	71.76	71.76
	.002	16.50	26.55	24.40	15.78	25.11
	.003	5.74	5.74	4.30	5.02	6.45
	.004	5.31	4.30	3.15	4.30	6.45
	.005	4.95	5.02	3.58	5.02	7.17
	.007	4.30	3.58	2.58	3.58	6.45
	.010	3.72	3.17	1.93	2.87	4.30
	.015	3.76	3.15	1.96	3.58	5.74
350	0	77.52	77.52	77.52		77.52
	.002	57.37	65.89	62.79		65.12
	.003	29.46	41.08	46.51		39.53
	.004	24.80	24.80	27.13		23.25
	.005	23.25	23.25	25.58		24.03
	.007	19.38	20.93	20.93		23.25
	.010	19.38	19.30	22.48		22.48
	.015	17.05	19.07	20.69		21.70

Table 3 (continued)

Temp.(°C)	Time (sec.)	A	B	C	D
300	0	84.29	84.29		84.29
	.002	77.54	81.76		79.23
	.003	72.49	76.70		75.86
	.004	67.43	72.49		70.80
	.005	63.21	69.12		68.27
	.007	58.16	63.12		61.53
	.010	53.10	60.69		59.00
	.015	48.88	53.94		53.10

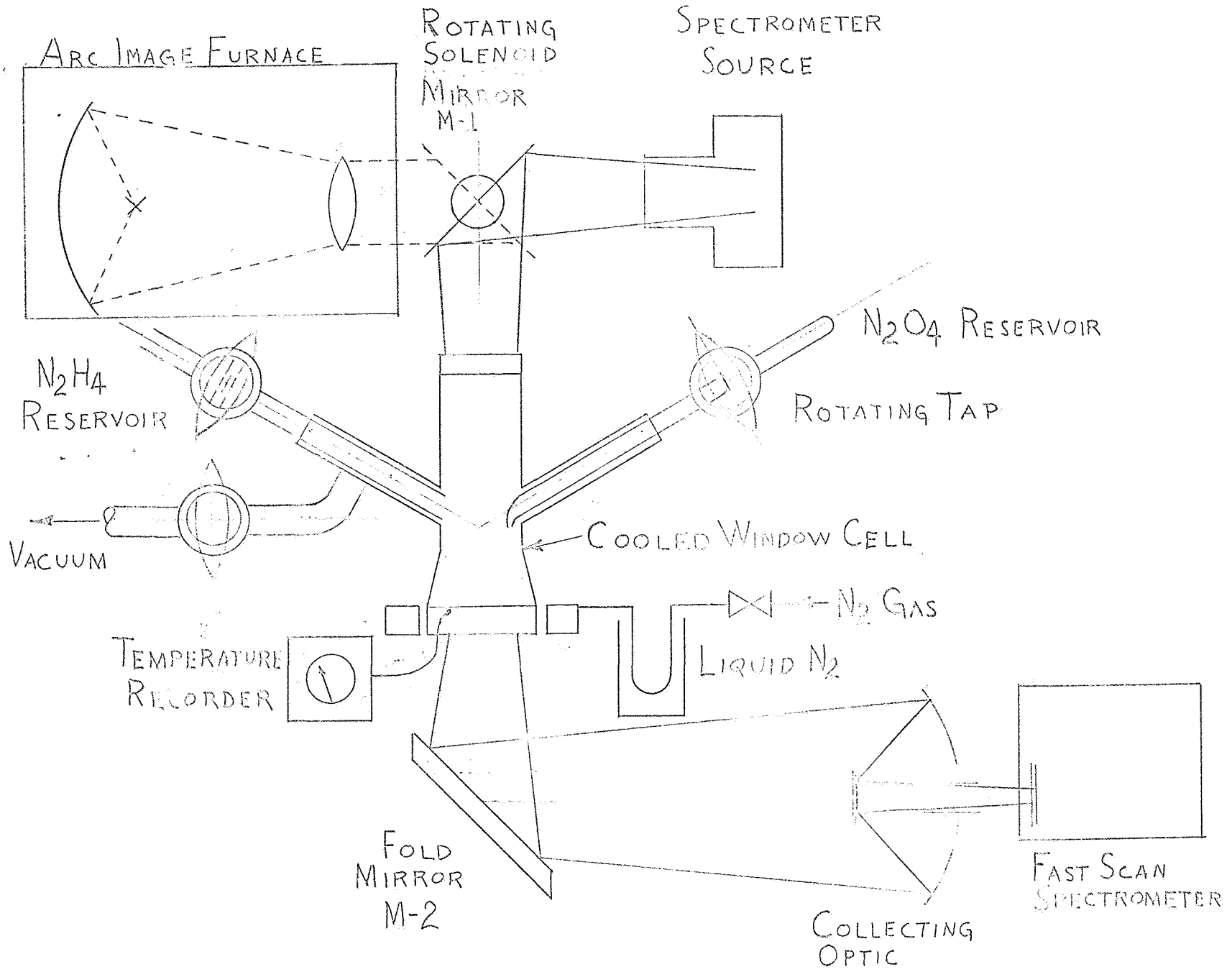

FIG. 1. OVERALL SETUP

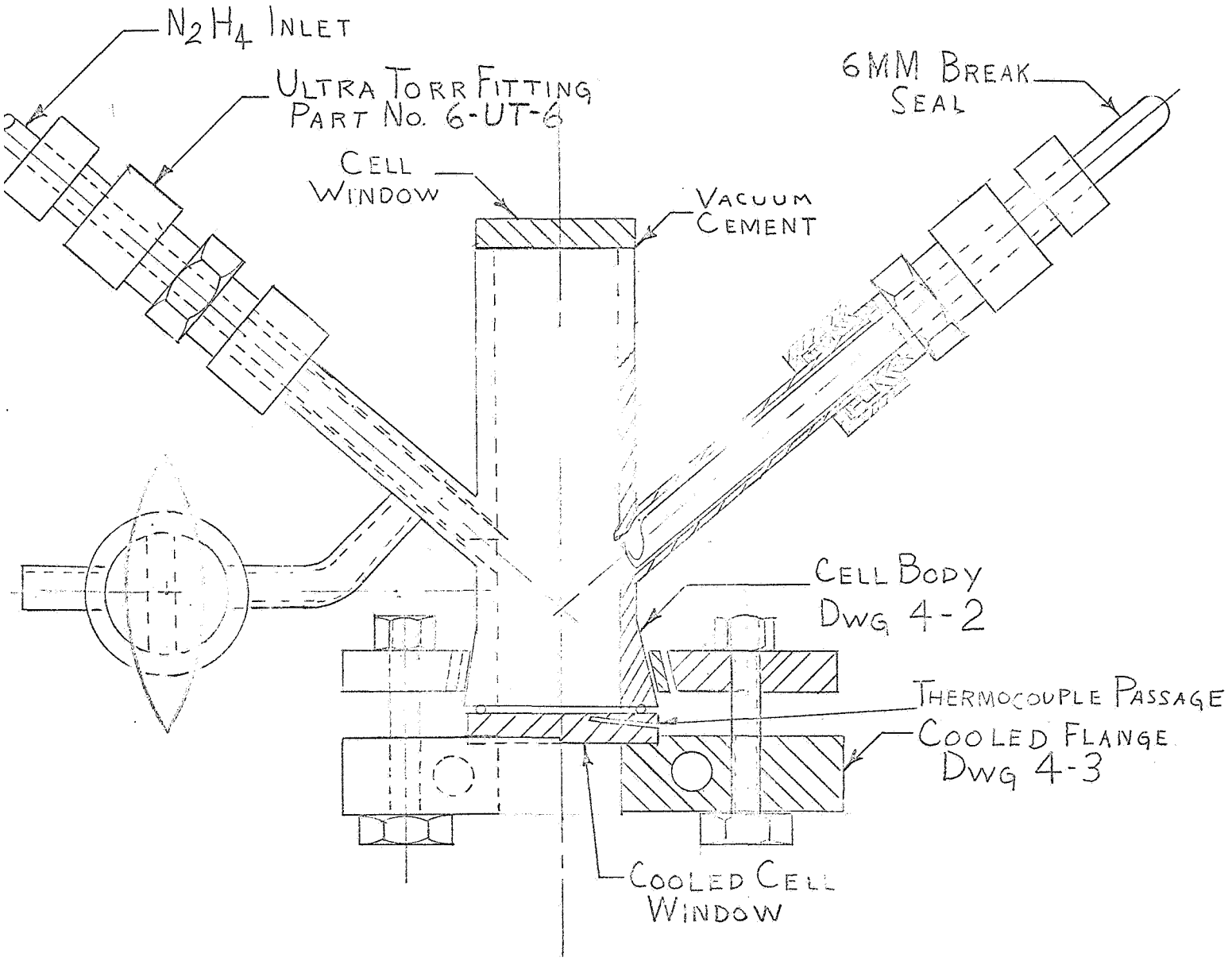

FIG. 2. Cell Assembly
G.R.K.
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