A PRELIMINARY DESCRIPTION OF THE CHEMICAL CAMERA

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Prepared for:

Jet Propulsion Laboratory
Pasadena, California

Contract No. 951573

Report No. 4001

September, 1966

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

CHEMATICS RESEARCH

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1. INTRODUCTION

The Chemical Camera is a device which can sample a high speed gas with submillisecond time resolution and provide samples for detailed study of the kinetics of chemical reactions. A preliminary design of this device and the experimental demonstration of its capabilites is described here in detail.

The Chemical Camera is designed to condense a portion of a gaseous beam sampled from a reacting gas without affecting the composition of the sample. This will provide a direct record which will permit study at a later time of a "slow-motion" reproduction of the chemical reaction as it occurred.

It is anticipated that the technique described herein will add a valuable tool to complement those already in existence. The capabilites of the Chemical Camera will make a unique contribution to the analysis of rapidly occurring reactions.

Entry of test gas into the Chemical Camera will be controlled by a blast shutter which will, upon command, open with millisecond response and remain open for a predetermined period of time; this time is adjustable from 0.1 msec. up to the period of time required for the cryostat to make one revolution (~12 msec.). The shutter will then close to make a vacuum tight seal, preventing destruction of the record on the drum by overwriting.

The instrument, described in Section 2 of this report, incorporates a cryopumped skimmer which has been designed to remove from the view of the rotating cryostat all portions of the gaseous beam which have undergone collision with the walls or otherwise become non-representative of the composition of the gaseous beam. Thus, the material frozen out on the rotating cryostat will have undergone no interactions after leaving the reaction zone except for the freezing itself.

The following sections and accompanying figures describe the construction, expected mechanical behavior, and proof tests of the device.

It is felt that the Chemical Camera as described here will surpass the behavior of any spinning cryostat in existence and is feasible for the investigation not only of shock tunnel experiments, but for other gaseous physical processes in which a detailed knowledge of the temporally resolved chemical reactions is important.

2. DESCRIPTION OF THE CHEMICAL CAMERA

2.1. General Considerations

The Chemical Camera is designed to select a sample from a supersonic gas stream with a minimum change in the chemical properties of the high velocity stream. This basic requirement places purely geometrical limitations upon the entrance port to the internal, spinning cryostat. In the form presented here, the device will allow passage of the external stream with no compressional disturbance affecting the incoming gas provided that the free stream Mach number is greater than four. The entrance port to the shutter mechanism is sized so that normal shock patterns on the shutter housing for Machnumber four or greater will not extend into the upstream cone of influence of the final skimmer diameter. Fig. 1 is a sectional view of the instrument, which consists of four concentric cylinders. The central cryostat spins at a nominal maximum speed of 5000 rpm. The cryostat is five inches in diameter so that a surface speed of 1320 in./sec. is achieved. A sample of the external gas stream of 0.200" diameter (~5mm) is to be accepted so that the resulting time resolution will be approximately 0.30 msec. Since the time resolution varies as the diameter of the projected orifice of the beam skimmer, this time resolution will be even finer for flows in which enough gas for analysis can be accepted by a smaller diameter. The cryostat is to be machined of stainless steel and heavily plated with gold in the region upon which the gas sample is to be deposited. The gold provides both an inert surface as well as a dense and highly conductive substrate upon which the sample can condense.

2.2. Support Equipment

The concentric cylinder surrounding the spinning cryostat is a liquid helium reservoir which supplies the helium cooled beam skimmer. The final skimmer is helium cooled to avoid skimmer interaction problems encountered in molecular beam experiments[1]. This skimmer defines the beam to be selected and provides a shield to the already deposited sample. A small stationery annular reservoir supplies this shield with refrigerent. Surrounding the two helium containing reservoirs is a nitrogen jacket which provides a radiation shield to energy emanating from the external cylindrical vacuum jacket.

A fast, squib (explosive cartridge) operated, valve is provided in the external vacuum jacket to expose the internally spinning cryostat to the beam for a desired period of time. The details of this shutter are shown in Fig. 2. Other access ports are provided to allow samples to be taken from the cryostat surface or to allow visual or other optical observations to be made on the deposited sample.

The central cryostat must operate in a vacuum (10^{-5} torr or better) and yet must spin at 5000 rpm. To achieve this, a cooled shaft seal utilizing carbonized teflon "O"-rings has been incorporated into the design, as shown in Fig. 3. An external pump will circulate oil through the seal block during motor operation. The shaft is driven by a one-half horsepower variable speed motor. The following discussion presents the details of the considerations which led to the major design decisions. Where the design incorporates either routine cryogenic engineering decisions or routine vacuum technology, a detailed description has not been given here.

2.2.1. Spinning Cryostat

The time resolution, τ , can be determined from the relation

$$\tau = \frac{\delta}{\pi d N} \qquad (1)$$

where δ is the skimmer diameter, d is the cryostat diameter, and N is the angular speed. Fig. 4 indicates the expected time response; as can be seen, millisecond resolution time is quite easily achieved.

In addition to the resolution time, it is necessary to provide sufficient duration so that the flow can be sampled during the entire useful flow period. The maximum duration of the test is just 1/N, where N is the rotation rate in revolutions per millisecond. If the shutter were to require 2 msec. (very long) to open and to close and a run of at least 10 msec. is required, the drum speed must not exceed 5000 rpm.

2.2.2. Mass Flux Capacity

As described above, the skimmer system consists of a preskimmer which is nitrogen cooled and a final helium cooled skimmer. Only weak Mach waves will be generated in the gas being collected so that virtually no "processing" will occur after the gas enters the cryostat port. Shock waves will exist at the shutter orifice edge but will be close to the surface, especially if the Mach number is four or greater. Once a quantity of gas enters the port, a decrease in the collision rate

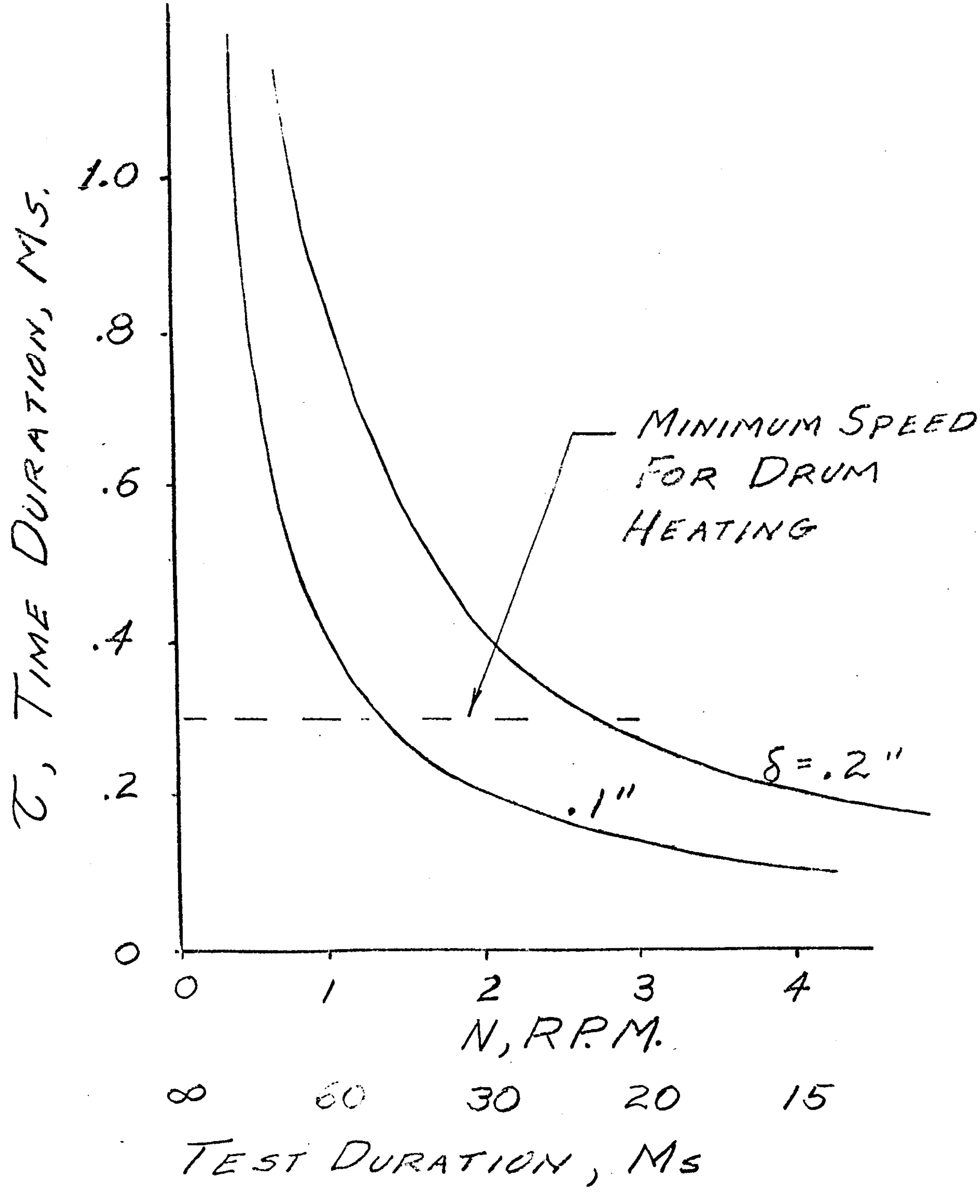

Figure 4. Test Time Resolution for theChemical Camera

will occur in the gas since the gas surrounding the central stream tube will be skimmed off. This is not expected to cause any spurious chemistry.

The gas entering the cold skimmer must be deposited upon the central cryostat. If the free stream gas density is ρ_∞ and the velocity is V_∞ we can write

$$Q \cong \frac{1}{2} \rho_\infty V_\infty^3 A_s \tag{2}$$

where A_s and Q are the skimmer area and the total heat flux, respectively. The specific kinetic energy is approximately

$$\frac{1}{2} V_\infty^2 \cong h_s \tag{3}$$

so that

$$Q \cong \rho_\infty V_\infty h_s A_s \tag{4}$$

$$Q \cong \sqrt{2}\, \rho_\infty h_s^{3/2} A_s \tag{5}$$

in which appropriate units are used. For a shock tunnel, h_s depends upon the strength of the initial shock in the driven tube, while ρ_∞ is a function both of the shock strength and of M_∞.

The ability of the cryostat to absorb this heat flux and freeze the deposited gas depends upon the ability of the cryostat to conduct away the flux. The quasi-steady heat flux problem corresponds to a finite circular source moving along a cooled surface with velocity v, the surface velocity of the drum. If we consider a more restrictive case to be the instantaneous heat release Q/A over a semi-infinite plane, a possible temperature solution[2] is

$$T = T_0 + q\left(\frac{t}{\pi K}\right)^{\frac{1}{2}} e^{-\frac{z^2}{4Kt}} - \frac{qz}{2K}\,\mathrm{erfc}\,\frac{z}{2\sqrt{Kt}} \qquad (6)$$

where K is the diffusivity and Z is the depth into the surface and q is the heat flux divided by the density-specific heat product for the drum material. Eq. 6 indicates increasing temperature for $t > 0$.

The question now is, how long can this surface remain at a sufficiently low temperature so that the incoming stream will stick. McDermott[3] has found that the surface will continuously pump until a critical temperature of 30° to 40°K is reached. At this point, a catastrophic change in the flow field occurs. A shock "pops" out from the surface and the cold surface ceases to pump efficiently. Now to use Eq. 6, we assume that $z \to 0$, so that

$$T \cong T_0 + \frac{Q/A}{\rho c}\left(\frac{t}{\pi K}\right)^{\frac{1}{2}} \qquad (7)$$

Clearly, we need K to be a maximum as well as ρc. For this reason, gold has been selected as the surface material of the cryostat.

The maximum design value of stagnation enthalpy will be selected as 6000 BTU/# with a P_t maximum of 15,000 psi and M_∞ of 10 yielding a free stream density of 1 x 10^{-5} g/cm^3. The heat flux is spread over an area approximately 10 times that of the accepting skimmer (i.e., the flow expands in the cryostat); however, we will neglect this. Using the data for gold, the surface temperature can be calculated to be less than 30°K for $t < 0.3$ msec. The total mass collected in 0.3 msec. will be, for the above case,

$$M = \rho_\infty u_\infty A \Delta t \qquad (8)$$

or, approximately 0.25 mg. per 0.3 msec. If the density of material is approximately 0.5 g/cm^3, the thickness will be 0.02 mm so that the temperature drop through the frozen layer will be minimal.

The heat transfer estimates given here are slightly conservative. Further, the temperature rise is more easily reduced by expanding the flow to a Mach number greater than 10. This can be accomplished by moving the helium skimmer entrance farther downstream and by decreasing the port diameter of the nitrogen skimmer. Since the device appears to be feasible in its present form and since the present desire is to maintain an unperturbed gas sample, the present arrangement is deemed best. It is interesting to note that because of the short times involved, there will be no extra boiling of the helium during the test. The inner wall simply will not feel the energy flux for several hundred milliseconds.

All angles on the skimmer are such that attached shocks will where $\ddot{x}$ is the shutter acceleration, M is the mass, D is the driving rod diameter, P_g is the pressure generated by the squib, f is the friction factor of the "O"-ring and F_n is the stagnation pressure of the supersonic free stream. Again, we assume M = 10, P_s = 15,000 psi, and a stagnation enthalpy of 6000BTU/#. When Eq. 9 is integrated and an acceleration length of 1.25" is assumed, the shutter opening time is 0.6 msec. after the acceleration period of 2 msec. The duration of open position is controlled by the length of a slot cut in the shutter face. At the end of its travel, a rubber dampener and a latch are provided to prevent rebound. The valve remains in the fired position until reset for another test. The sealing "O"-ring will have an extremely short life, probably not more than one or two shots.

A considerable number of alternate shutter designs have been considered; however, all have been discarded in favor of this relatively straightforward design.

2.3. Preliminary Procedure for Operation of the Chemical Camera

The following is a narrative description of a typical experiment. A detailed checklist with proper sequencing will be provided after some experience has been gained with a working model of the Chemical Camera.

The shock tunnel will be prepared for firing. The control of exact firing is of importance because of the requirements that the shutter start at a prescribed time relative to shock initiation. Exact knowledge will exist on the shutter behavior after statistical calibration by experimental firings have been made with representative squibs.

First the shock tube driver will be prepared and the driven tube loaded. The Chemical Camera will have been located in the test section with the shutter port centered upon the region of interest. (The design described in this report will sample only one streamline, however, a simple modification will allow sampling of several locations at once.) A vacuum will have been established in the device before the nozzle and dump tank evacuation. Also, nitrogen will have been placed in the external jacket at least one-half hour prior to the test. The following events will occur immediately prior to firing.

The upper and central helium reservoirs will first be filled with one liter each of nitrogen. They will then be emptied through the same transfer lines. These reservoirs will then be refilled with helium by means of a small vacuum insulated transfer tube of suitable design. (These are commercially available or can be constructed for approximately $100 per foot.) A carbon resitor, located in the upper helium reservoir, will indicate a stable helium level in that location. It will be assumed that the central cryostat is also filled at this time. If a small amount of nitrogen is left in these dewars, it will simply be frozen by the helium. Both helium dewars will be maintained at helium temperature for at least 15 minutes, which will require a second filling of the upper reservoir. After this has been done, the experiment is ready to be performed.

The seal coolant pump will be started and the drive motor will bring the central cryostat up to speed. The speed of the cryostat will be determined by shining a small beam of light on the teeth of a timing belt drive wheel placed above the active belt pulley. The faces of all except one of the teeth on this pulley will have been polished. The unpolished tooth will be blackened so that when the output signal of a phototube sensitive to light reflected from the gear teeth is displayed on an oscilloscope, the spacing of the light blips will determine the rotational speed. The missing blip will act as a register to determine the angular position of the drum during the test.

Another light beam will be reflected from the shutter face and the output of a phototube observing this will be displayed on the same oscilloscope used for the timing (Tektronix 502 dual beam or better). During the initial calibration of the shutter behavior, sufficient knowledge will be obtained to predict when the shutter will open after each squib firing. It is expected that this time will be short compared to the time required to fire the shock tube. Assuming that this is so, the squib will be actuated by a properly delayed signal derived from a heat transfer gauge placed on the shock tube wall. This same signal will trigger the scope.

Once the shutter is actuated it will traverse the port, allowing passage of the active test gas. The shutter is provided with a non-rebound latch and an energy absorber. The spin motor will be turned off and the cryostat allowed to come to rest. The central cryostat and the nitrogen jacket will be refilled. The tunnel can then be opened and access gained to the Chemical Camera.

Now, either samples will be scraped from the surface of the drum for ESR or other tests, or optical measurements will be made on the surface. The time at which a given sample was deposited will be determined by its relationship to the blackened gear tooth and the rate of rotation of the cryostat.

3. CHEMICAL KINETICS

3.1. Demonstration of the Presence of Free Radicals on the Rotor

The ability to trap free radicals on a cryogenic surface has been noted by many authors and has been well reviewed[5]. Examples of more current work are available in the proceedings of international meetings[6,7].

Since the activation energy for recombination of free radicals (or of any active species) is very low (approximately the activation energy for diffusion), the reaction must be prevented by the isolation of the free radicals from each other. This isolation may be accomplished either by freezing the active species in an inert diluent or in the undecomposed parent material.

To prove that the Chemical Camera is capable of trapping free radicals, the hydrazoic acid system has been chosen for the ease of production, trapping, and identification of free radicals. Although this system is chemically complex and is not completely understood, it is generally agreed that the thermal or photochemical dissociation of hydrazoic acid takes place by a free radical mechanism and that the blue color observed by the cryogenic trapping of the dissociation products is caused by the presence of free radicals[8-17]. The conflict in precisely which free radical is responsible for the blue color has not been resolved, but has variously been ascribed to NH, N_2H, $(NH)_3$, $(NH)_4$, etc.

Therefore, pyrolysis of hydrazoic acid (HN_3) in a flow tube apparatus followed by freezing out of the colored free radical products on the cryostat surface will provide a simple and convincing demonstration of the stabilization of free radicals on the rotating cryostat. Since the radicals produced by the decomposition of hydrazoic acid appear to be quite stable up to 123°K[13,15] this experiment can easily be performed using liquid nitrogen as the refrigerent in the cryostat and skimmer.

3.1.1. Experimental Conditions

The production and pyrolysis of hydrazoic acid may be performed in a glass apparatus as shown schematically in Fig. 5. Hydrazoic acid will be generated by adding concentrated sulfuric acid dropwise into the reaction bulb which contains sodium azide. The gaseous hydrazoic acid so generated will flow into the storage bulb. When the desired amount of acid has been produced, as monitored on a pressure gauge, the stopcock separating the reaction and storage bulbs will be closed and the reaction bulb refrigerated with liquid nitrogen to prevent further reaction. (Since HN_3 is both toxic and explosive, it is not advisable to generate more material than is immediately required.) Next, the hydrazoic acid gas is permitted to flow through the pyrolysis furnace. Since the temperature in the furnace will exceed 1000°C, this portion of the vacuum system will be fabricated of quartz.

The simple, qualitative observation of a blue coloration on the drum will suffice to demonstrate the stabilization of free radicals. Color photographs will be used to document this ability of the rotor to store and stabilize free radicals.

When warmed to about 123°K, the blue material is able to diffuse and the free radicals which are present undergo a chemical reaction to

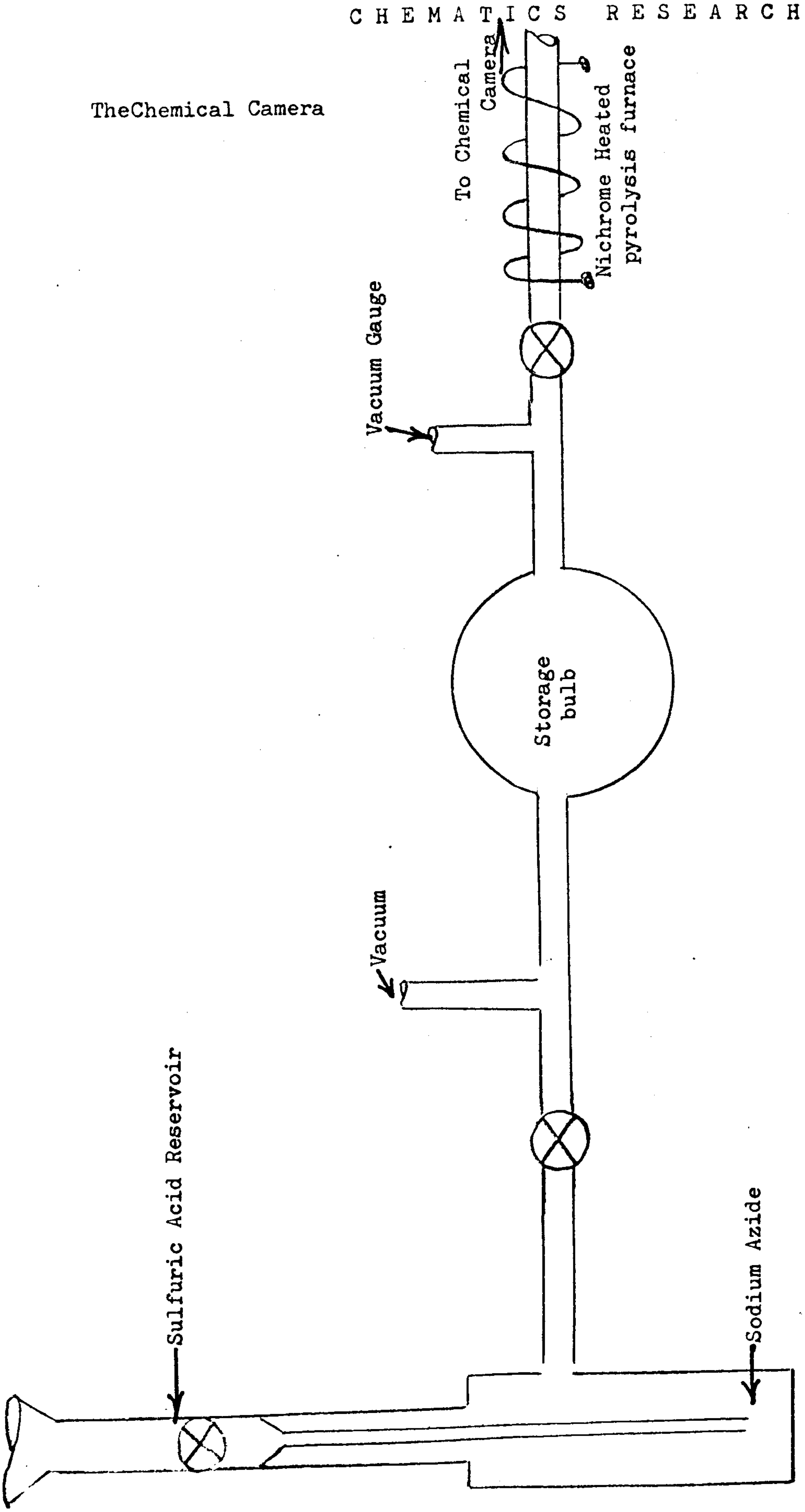

Figure 5. Apparatus for the Decomposition of Hydrazoic Acid

form ammonium azide, a white solid. Hence the blue color abruptly disappears. The observation of this abrupt color change is a further indication that the free radicals which were present at the lower temperature have become unstable and have reacted.

3.2. Observation of Chemical Kinetics

In order to demonstrate convincingly the capacity of the Chemical Camera to record the chronology of a chemical reaction, a simple system has been selected in which the progress of the reaction will be traced by the observation of a color visible to the human eye. The chemical reaction to be studied is the recombination of colorless iodine atoms, I, on a third body to produce the highly colored iodine molecule, I_2. The third body, M, can be an inert gas, iodine molecules, or the walls of

$$2I + M \rightarrow I_2 + M \qquad (10)$$

the reaction vessel. This system is particularly convenient also because iodine atoms stabilized at liquid nitrogen temperatures in a suitable matrix. The atoms can conveniently produced by flash photolysis. The reacting mixture will be sampled continuously from a leak and frozen out on the rotating drum of the Chemical Camera. The mechanical shutter, coordinated with the flash dissociation of the iodine molecules, will close after a single revolution of the cryostat to form a vacuum seal, thus preserving the integrity of the record stored on the drum. Hence, the composition of the material frozen on the rotating cryostat will vary with the position of the drum in the same manner as the composition of the gas varies with time for the period of one revolution of the drum.

3.2.1. Recombination of the Iodine Atoms

The combination of iodine atoms on a third body has been studied extensively[18-22] and, although there is some uncertainty about the details of the rate of this reaction, there is sufficient agreement among the determinations to permit the use of this reaction to demonstrate the capabilites of the Chemical Camera.

The mechanism of this reaction appears to be[23] that given by Eqs. 11 and 12 in which M is a third body, i.e., the wall of the reaction vessel,

$$I + M \rightleftharpoons IM \qquad (11)$$

$$IM + I \rightarrow I_2 + M \qquad (12)$$

a molecule, or an atom. Under the experimental conditions of relatively high pressure (about 1 atm.) and high dilution of iodine molecules with an inert diluent (about 1000 Xe atoms to 1 iodine molecule initially), the xenondiluent will certainly be the most important third body. However, although iodine molecules may be expected to contribute to the rate because of their high efficiency[18] as third bodies in the combination of iodine atoms, because of their low concentration under the experimental conditions described below, this may be neglected.

The rate of iodine atom recombination in the presence of Xe is given by Eq. 13, in which terms in parentheses indicate the concentration of the species enclosed therein.

$$-\frac{d(I)}{dt} = k_{Xe}(I)^2(Xe) + k_{I_2}(I)^2(I_2) \qquad (13)$$

Previous measurements[20] have indicated that $k_{Xe} \cong 10^{10}$ and $k_{I_2} \cong 10^{11}$ $\ell^2 \text{mole}^{-2} \text{sec}^{-1}$. Under the conditions designed for performance of this experiment, the initial concentration of iodine molecules will be approximately 0.1% that of the xenon atoms. Furthermore, the intensity of the flash will be adjusted so that some 90% of the iodine dissociates, making the Xe/I_2 ratio approximately 10^4, so that

$$k_{Xe}(I)^2(Xe) \big/ k_{I_2}(I)^2(I_2) \cong 10^3 \qquad (14)$$

in which case the second term on the right hand side of Eq. 13 can be neglected with respect to the first term.

In the experiments described below, conditions will be adjusted so that the recombination reaction will proceed approximately to two-thirds completion in one revolution of the cryostat. In this way, sensitivity will be increased since this is the time during which the reaction proceeds most rapidly.

A further advantage of the iodine system is that the active species is colorless and the extinction coefficient of the iodine atom (perhaps difficult to measure) is not required since all analysis is based upon the determination of the amount of stable iodine molecules.

3.2.2. Experimental Apparatus

The apparatus will consist of an argon flash lamp and appropriate power supply to furnish radiant energy to the vycor reaction vessel portion of the vacuum system, as illustrated in Fig. 6. A small orifice will be located in the end of the cell from which a gas sample will be continuously taken into the low pressure region of the liquid nitrogen cooled cryostat. The shutter will be opened in syncronization with the firing and subsequent decay of the flash lamp.

The cell will be filled to a predetermined pressure with a mixture of xenon and iodine of known composition with the shutter closed. During the time prior to the photolysis, the gases which leak out of the cell are pumped away by auxiliary pumps which maintain the pressure below 10^{-5} torr in the vicinity of the shutter. Upon opening the shutter, atoms and molecules flow, virtually without collisions, to the cryostat where they are frozen out.

3.2.3. Results and Interpretation

The light from the flash lamp will dissociate some 90% of the iodine molecules. Light of wave length shorter than 4995 Å produces excited atoms[19] in addition to dissociating the molecules. However, these excited atoms are probably deactivated quite rapidly relative to combination because no difference is observed in the rate of combination of atoms produced by radiation of wave length less than 4995 Å and those produced with less energetic radiation which yields only

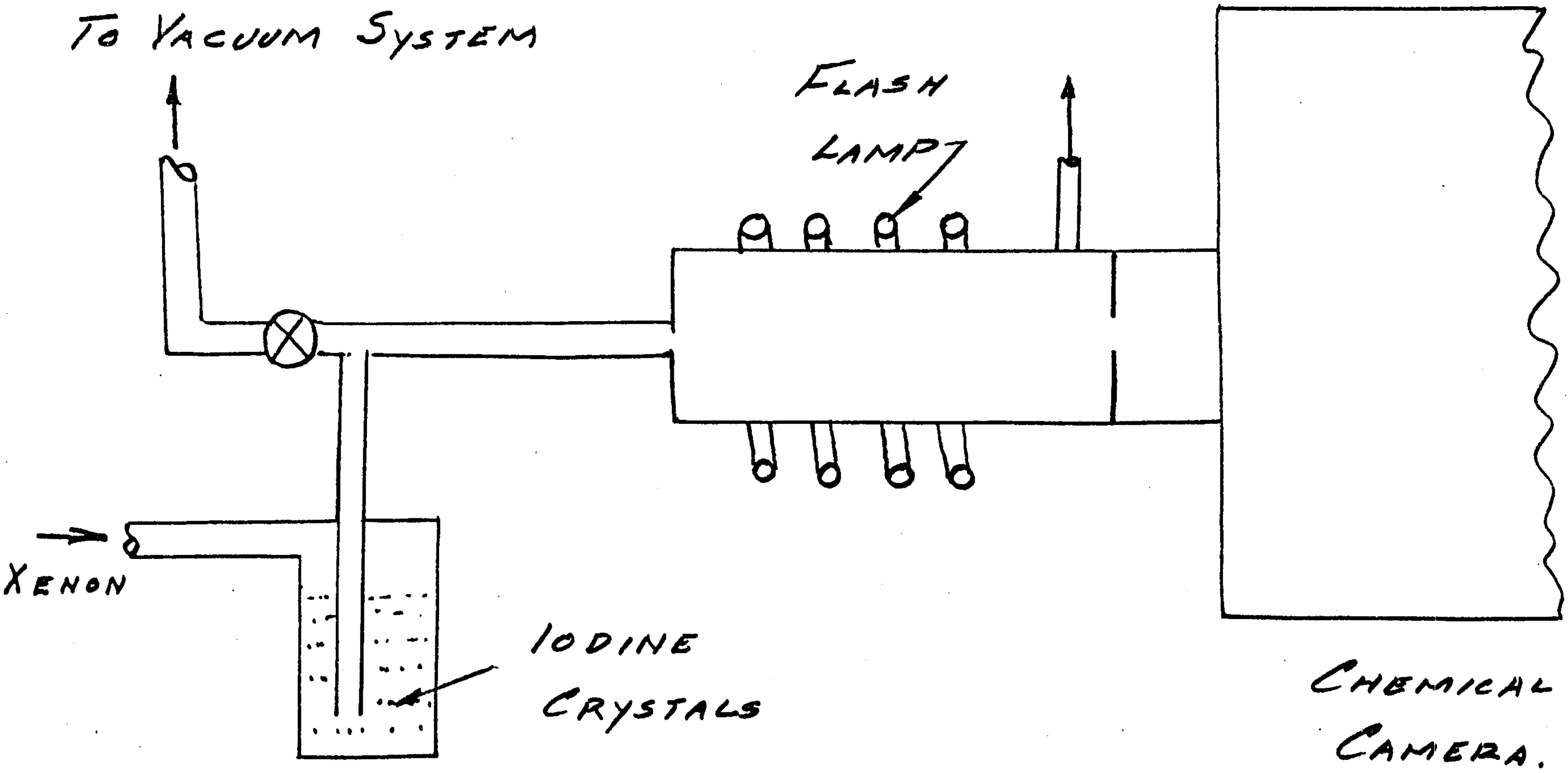

Figure 6. Apparatus for the Flash Photolysis of Iodine Molecules to Demonstrate the Utility of the Chemical Camera in Chemical Kinetics Studies

ground state atoms.

Since the xenon is essentially transparent to the radiation produced by the flash lamp, no radiation is absorbed and the slight increase in temperature of the gaseous system will be mainly due to the energy imparted to the atoms of iodine in excess of the dissociation energy. Since the mixture is dilute with respect to iodine, the overall temperature in this system will not be changed by more than a few degrees[23] by the incident radiation. Hence, the flash produces the equivelent of a mixture of iodine atoms and iodine molecules immersed in a xenon bath. After the average time required for the particles of this system to undergo three collisions (10^{-10} sec.) the system regains thermal equilibrium. The only departure from equilibrium at this point is the inordinately high concentration of iodine atoms so that the recombination of these atoms occurs in a very well characterized environment.

The first gas packet to be frozen out on the rotating cryostat will be the gas that has just received the radiant energy from the flash lamp. The shutter which prevented the gas from reaching the cryostat opens just as the lamp has decayed. Since dissociation of the iodine occurs in less than 10^{-12} sec. after the light is absorbed, the gas may be considered to dissociate with a time constant which is exactly parallel to the output of the flash lamp. Naturally, this will vary with the design of the lamp and the power supply, but it can easily be made[19] less than 100 μsec. in width, which is less than the expected resolution for the current design of the Chemical Camera.

Thus we have a very simple system: Atoms are generated instantaneously in virtual thermal equilibrium with their surroundings and the production of iodine molecules by their recombination is followed by the increase in the optical absorption (color) of the material sampled from the cell as it plates out on the rotating cryostat in an angular position which corresponds to the time at which it left the cell. Since pressures outside the cell are very low (less than 10^{-5} torr) virtually no reaction is expected to take place after the gas leaves the cell. Hence the composition on the cryostat can be expected to be the same as it was when the gas sample left the reaction cell. After one revolution, the shutter closes to prevent further deposition over the material of interest. Hence, the first material deposited should be only slightly colored and the intensity of the color should increase monotonically with angle on the cryostat, <u>i.e.</u>, with the time it left the reaction cell.

The analysis of the data obtained from this experiment is straightforward. The rate of recombination of iodine atoms to form iodine molecules is given by Eq. 13, which reduces to

$$\frac{d(I)}{dt} = -k_{Xe}(Xe)(I)^2 \qquad (15)$$

and, since the concentration of xenon is constant throughtout the experiment, a new constant, $k' = k_{Xe}(Xe)$, may be defined so that Eq. 6 becomes

$$\frac{d(I)}{dt} = -k'(I)^2 \qquad (16)$$

The chemical equation governing the recombination is

$$2I = I_2 \tag{17}$$

so that mass balance considerations give

$$\tfrac{1}{2}(I) + (I_2) = (I_2)_o \tag{18}$$

where the subscript "o" demotes initial concentration and the non-subscripted expressions in parentheses indicate instantaneous concentrations.

Changing the variable in Eq. 16, subject to the relationship of Eq. 18, gives Eq. 19:

$$\frac{d(I_2)}{dt} = k'\left[(I_2)_o - (I_2)\right]^2 \tag{19}$$

which may be integrated to give

$$\left[(I_2)_o - (I_2)\right]^{-1} = k't + C \tag{20}$$

Hence a plot of the reciprocal of the quantity $\left[(I_2)_o - (I_2)\right]$ as a function of time should give a straight line whose slope is k'

Absorption of visible light is a direct measure* of the I_2

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*The absorption of molecular iodine does not precisely follow Beer's Law[24] so that deviation from ideality must be taken into account in the interpretation of these data. Also, the spectrum is a function of temperature[25] so that the wave length chosen for spectrophotometry will depend upon experimental conditions.

concentration so that (I_2), as required by Eq. 20, may be determined optically and related to the time of effusion from the reaction cell by measurement of its angular position on the drum.

Should the material frozen out on the drum scatter light strongly attempts will be made to produce an organic glass by adding hydrocarbons to the mixture of gases in the cell. The specific hydrocarbons will be chosen from among those known glass formers which do not absorb in the region of interest. Alternate approaches include the reaction of the trapped iodine atoms with hydrogen atoms to produce hydrogen iodide as an identifiable derivative or the use of ESR spectroscopy.

3.3. The Use of Liquid Helium as a Refrigerent

After the characteristics of the Chemical Camera and its component parts have been determined by the procedures outlined in the previous sections of this report, its ability to operate using liquid helium as the refrigerant will be demonstrated by repeating the specific reaction rate constant for the recombination of iodine atoms, as described in Section 3.2. In this case, the rotating cryostat and the upper helium reservoir will be cooled to the temperature of liquid helium, utilizing the techniques of Section 2.3.

In this way, the data obtained at liquid nitrogen temperature can be compared with that obtained when liquid helium is used as the refrigerant. This comparison should provide data to permit evaluation of the degree of stabilization of iodine atoms at 77°K.

4. CONCLUSIONS

A spinning cryostat, referred to herein as the Chemical Camera, has been designed to allow sampling of a supersonic gas stream. Detail and layout drawings have been made and are presented with this report. The entire unit is compatible for use inside the JPL 43 inch diameter shock tunnel. The design incorporates features to allow use with liquid helium.

The ultimate time resolution of the device as it is now designed is 0.3 milliseconds with a test duration of 12 milliseconds. The resolution can be increased by a factor of three by replacing the 5mm final beam skimmer with a 1 to 2 mm skimmer. The final skimmer is helium cooled to avoid aerodynamic problems associated with molecular beam skimmers.

Two experiments have been designed to allow experimental verification of the design feasibility. These experiments will verify both the ability of the device to freeze free radicals and to follow the time history of a chemical reaction (the recombination of iodine atoms). A preliminary operating procedure has been described. This procedure has been evolved by considerations based upon the calculated performance of the device. Final procedures must be obtained after a working model has been constructed and experience has been gained in its operation.

The tests described in the body of this report are to be performed first using liquid nitrogen as the refrigerant. After successful operation has been achieved in this temperature range, the experiments will be repeated using liquid helium to allow verification of the chemistry and to demonstrate the utility of the instrument when liquid helium is the cryogenic liquid.

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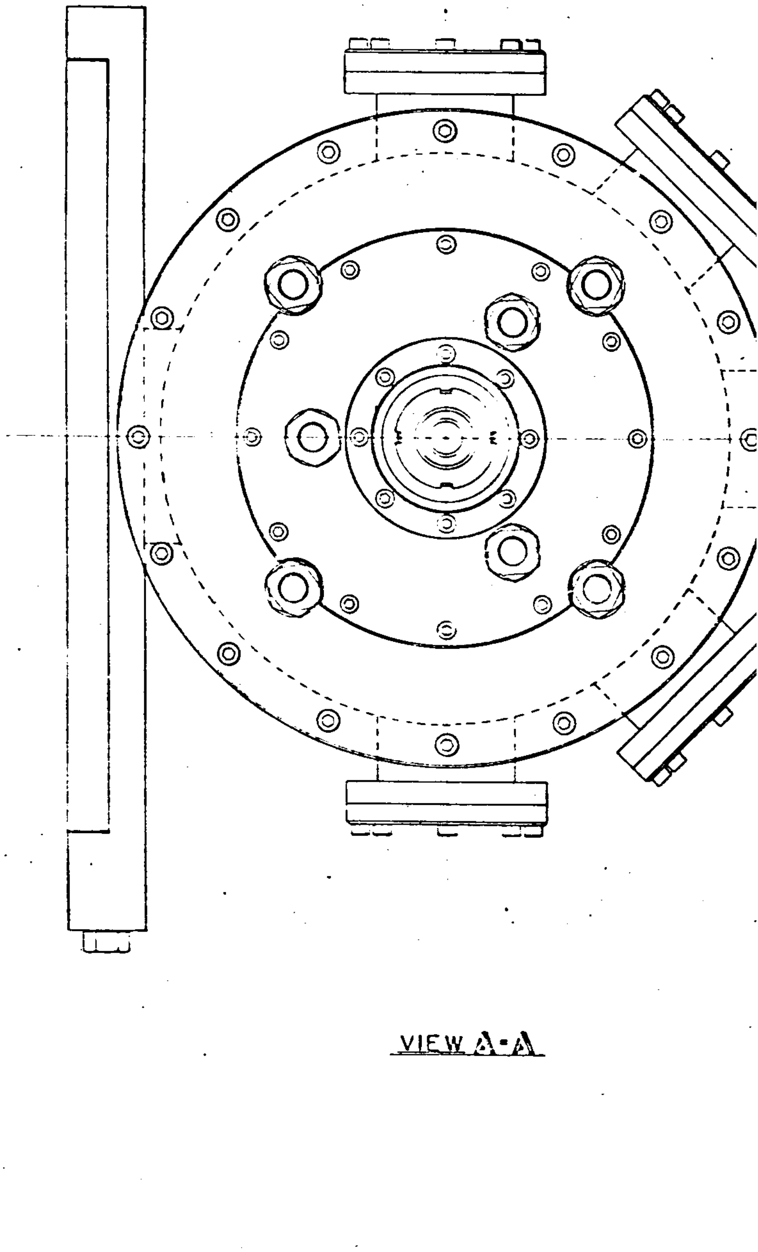
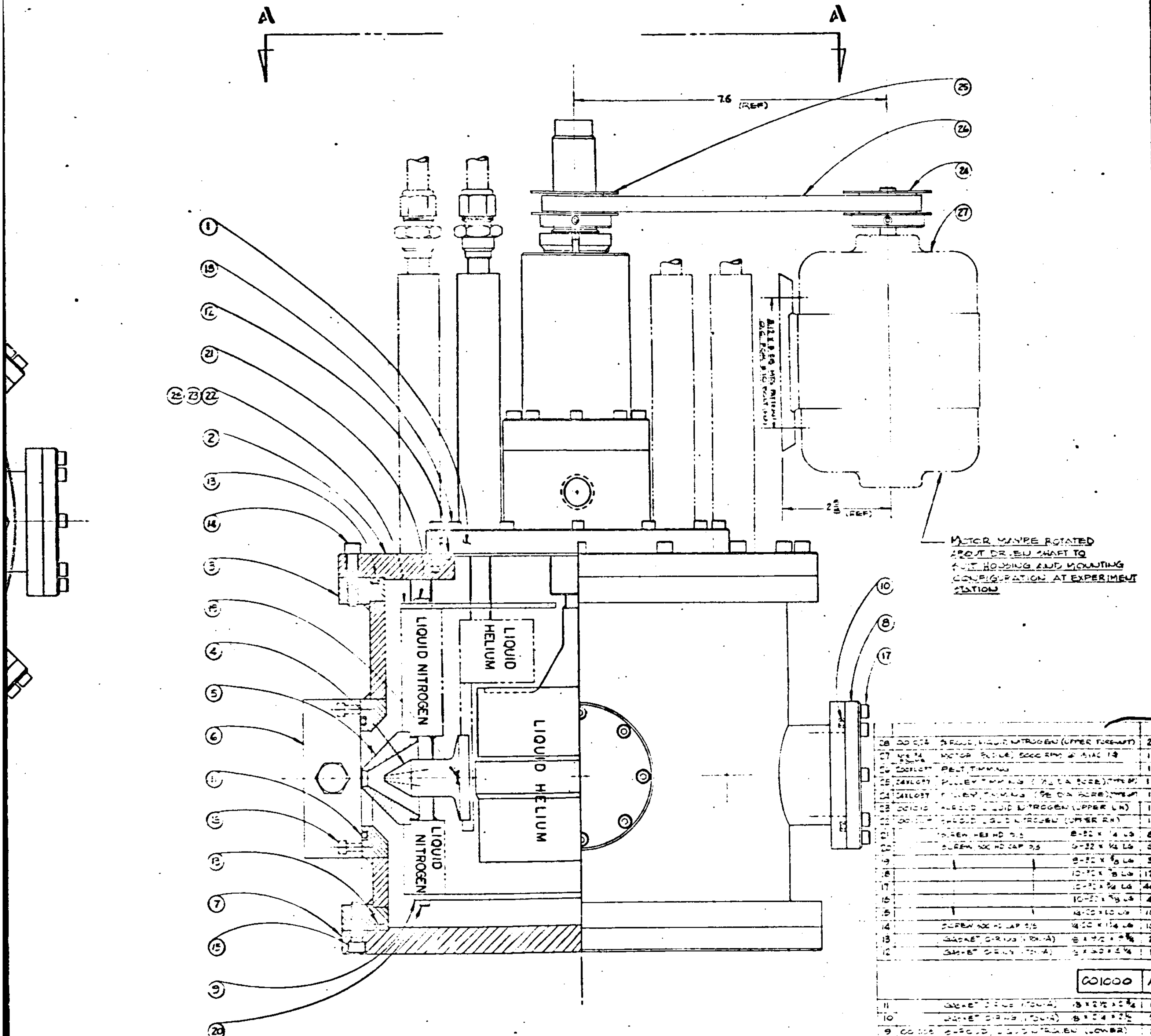


VIEW A-A

/



MOTOR MAY BE ROTATED ABOUT DRIVEN SHAFT TO SUIT HOUSING AND MOUNTING CONFIGURATION AT EXPERIMENT STATION

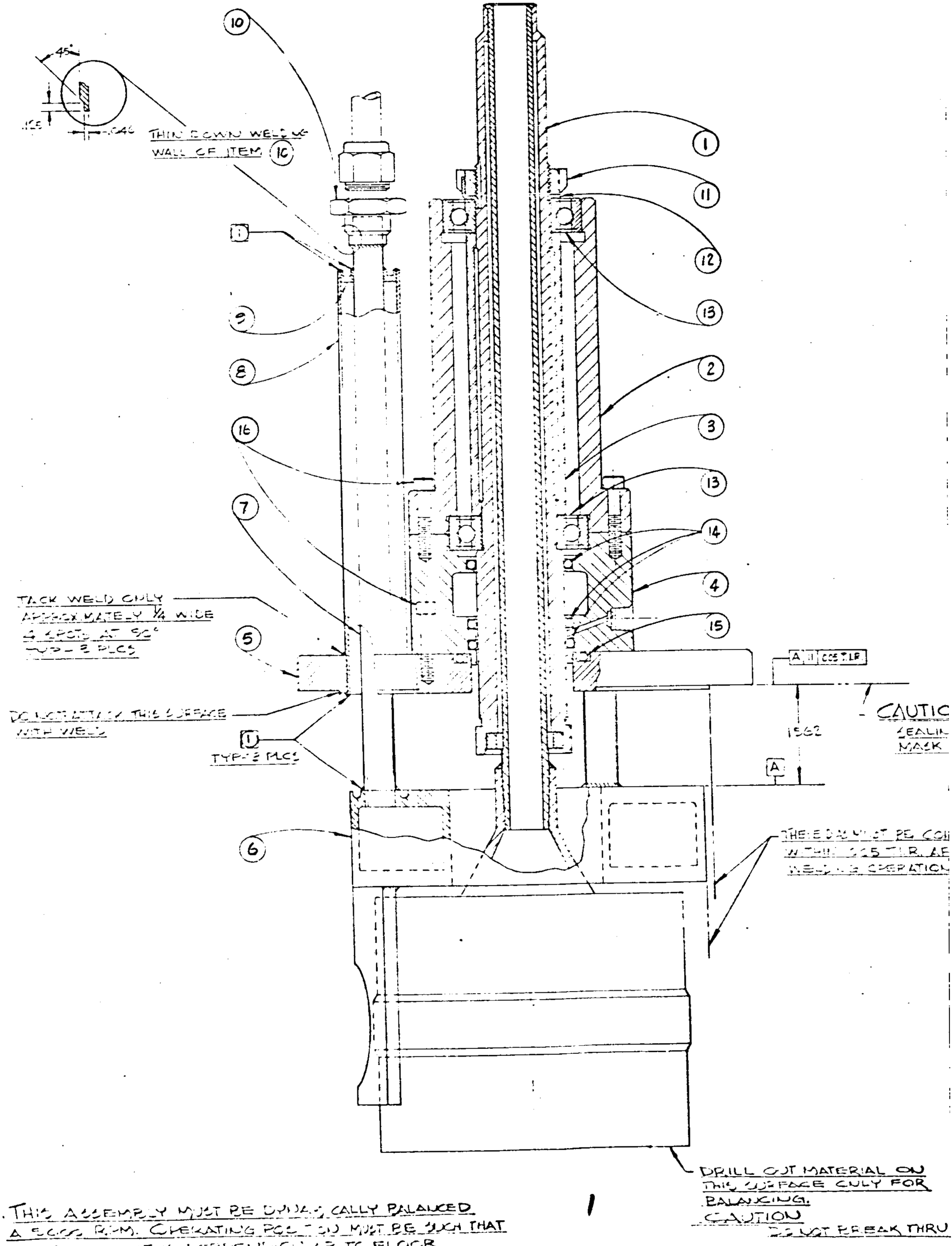
ITEM	REF DWG	DESCRIPTION		REQ
28	00 024	SHROUD, LIQUID NITROGEN (UPPER FOREWARD)		2
27	ME 24	MOTOR, PULSE, 5000 RPM @ 115AC 1Φ		1
26	2XL037	BELT, TIMMING		1
25	24XL037	PULLEY TIMMING (¼ DIA BORE)(TYPE B)		1
24	24XL037	PULLEY, TIMMING (⅝ DIA BORE)(TYPE B)		1
23	001010	SHROUD LIQUID NITROGEN (UPPER LH)		1
22	00 [illegible]	SHROUD LIQUID NITROGEN (UPPER RH)		1
21		SCREW HEX HD S/S	8-32 × ¼ LG	8
20		SCREW SOC HD CAP S/S	6-32 × ¼ LG	6
19			8-32 × ⅜ LG	3
18			10-32 × ⅞ LG	12
17			10-32 × ¾ LG	40
16			10-32 × ⅝ LG	4
15			¼-20 × 1 LG	16
14		SCREW SOC HD CAP S/S	¼-20 × 1¼ LG	16
13		GASKET, O-RING (VITON-A)	⅛ × 7½ × 7¾	2
12		GASKET O-RING (VITON-A)	⅛ × 3 × 3¼	1
11		GASKET O-RING (VITON-A)	⅛ × 2½ × 2¾	1
10		GASKET O-RING (VITON-A)	⅛ × 2¼ × 2½	5
9	00 009	SHROUD, LIQUID NITROGEN (LOWER)		1
8	00 007	COVER, INSTRUMENTATION PORT		5
7	00 008	PLATE, VACUUM COVER		1
6	00 006	VALVE ASSY HIGH SPEED		1
5	00 005	SKIMMER NITROGEN		1
4	00 004	SKIMMER HELIUM		1
3	00 003	CHAMBER, VACUUM		1
2	00 002	RESERVOIR ASSY, LIQUID NITROGEN		1
1	001001	CRYOSTAT ASSEMBLY		1

001000 A

CHEMATICS RESEARCH
[illegible] CALIFORNIA

CHEMICAL CAMERA ASSY

E 001000 A



1. THIS ASSEMBLY MUST BE DYNAMICALLY BALANCED
A 5000 R.P.M. OPERATING POSITION MUST BE SUCH THAT
SPINDLE SHAFT IS PERPENDICULAR TO FLOOR
[illegible] (UNLESS OTHERWISE SPECIFIED)

ON
G SURFACE —
N ROUTING

CENTRIC
TER
D INDICATED

TANK

16		SCREW, SOC HD CAP S/S 10-32 x 1.0 LG	13
15		GASKET, O-RING (VITON A) 1/8 x 3/4 x 2.0	1
14	5DB 220	SEAL, GRAPHITE FILLED TEFLON (BAL SEAL ENGRG [illegible] CALIF)	3
13	[illegible]	BEARING, RADIAL (SPEC 7) (NEW DEPARTURE)	2
12	W-03	LOCKWASHER, BEARING (NEW DEPARTURE)	1

001001	A

ITEM	PART NO.	DESCRIPTION	REQ
11	N-03	LOCKNUT, BEARING (NEW DEPARTURE)	1
10	[illegible]-6-ESW	FITTING, STAINLESS STEEL (SWAGELOK)	3
9	001019	SPACER	3
8	001018-1	JACKET	3
7	001017-1	TUBE	3
6	001016	RESERVOIR ASSY, HELIUM	1
5	001015	PLATE, COVER, BASE	1
4	001014	MANIFOLD, COOLING	1
3	001013	SPACER, BEARING	1
2	001012	HOUSING, BEARING	1
1	001011	SPINDLE/HELIUM RESERVOIR ASSY	1

REVISED 8-29-66
Hickman 10-10-66
Tannenbaum 10/10/66

2

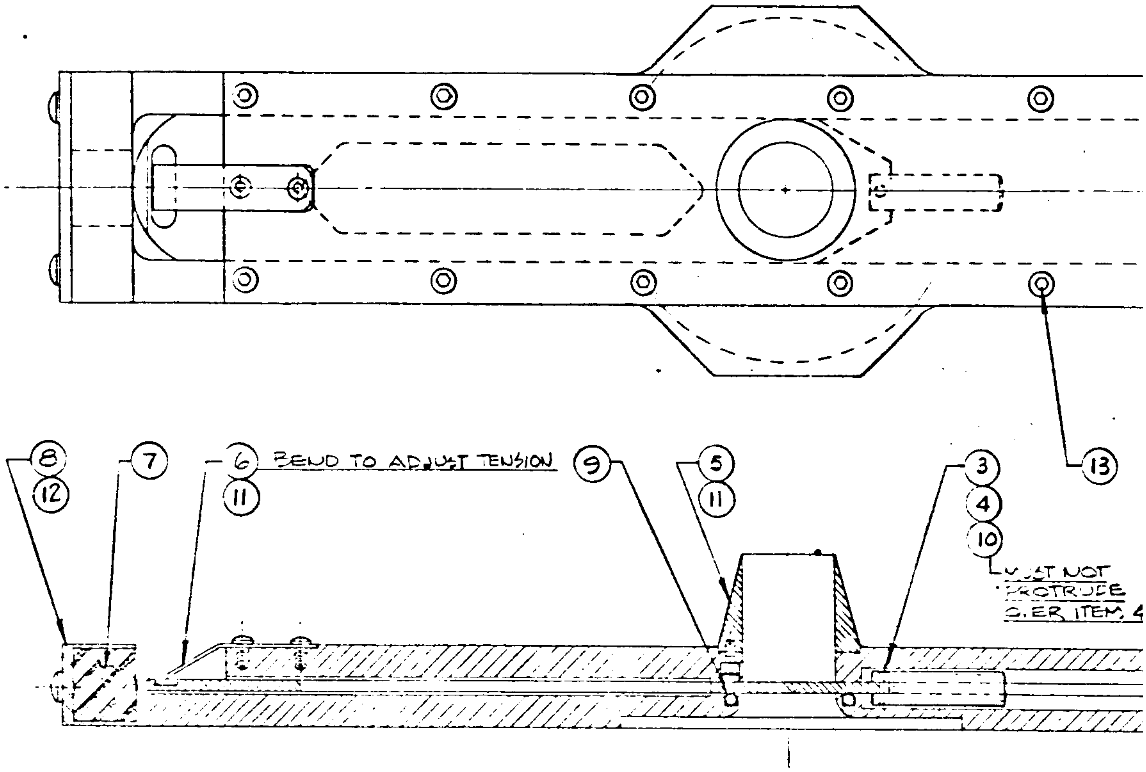
CHEMATICS RESEARCH
RESEDA CALIFORNIA

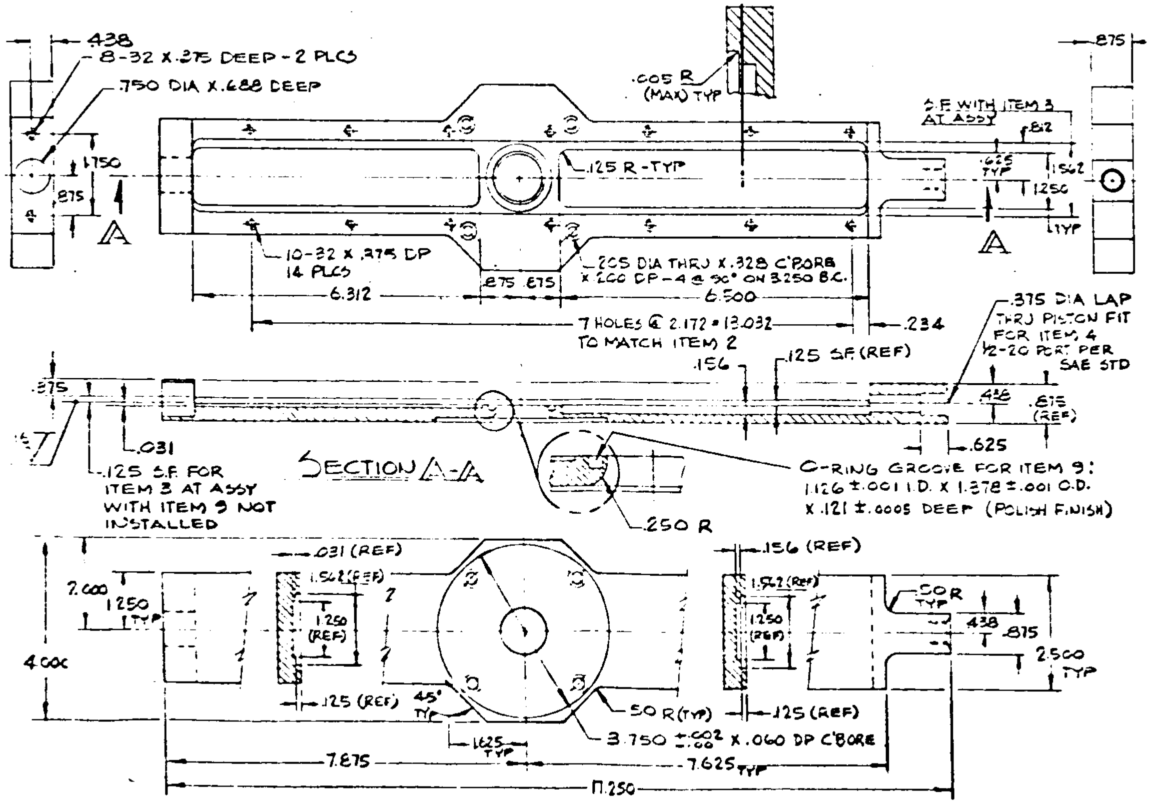
CRYOSTAT ASSEMBLY

001000

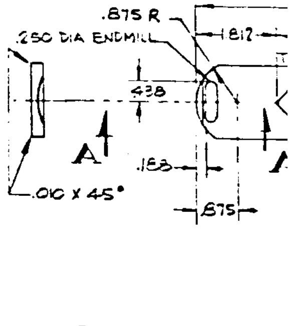
D 001001 A

1:1





DET ④ MAT'L: C.R.S. FINISH: CASE HDN .010, GRIND & BLACK OXIDE



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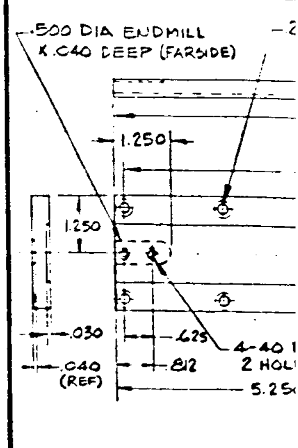
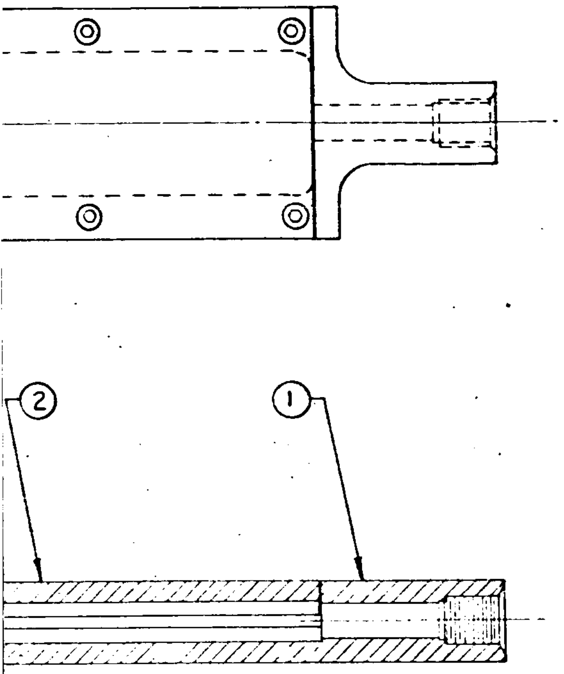
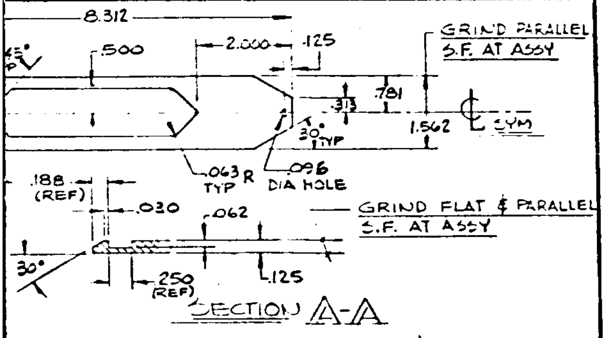
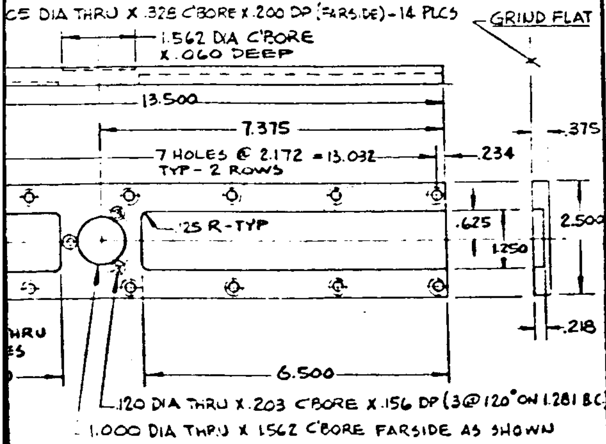


DET ② MAT'L: C.F

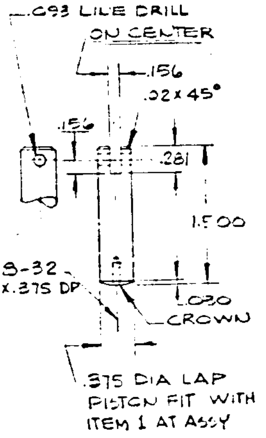




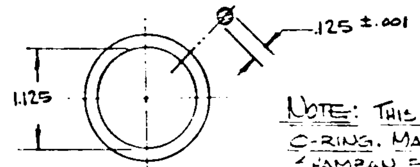
NIUM FINISH: GRIND & LAP



FINISH: CASE HDN .010, GRIND & BLACK OXIDE

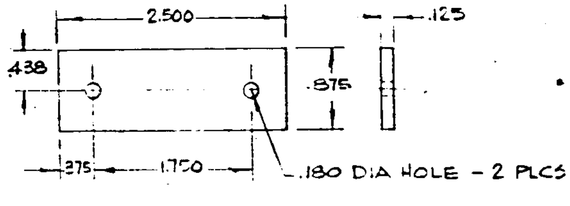


DET -4
MAT'L: TITANIUM
FINISH: GRIND & LAP

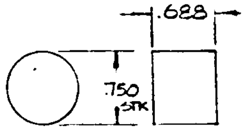


NOTE: THIS IS A SPECIAL SIZE O-RING. MAY BE MADE BY SHAMBAN ENGINEERING, L.A., VENDOR'S MFG TOLERANCE HOLDS

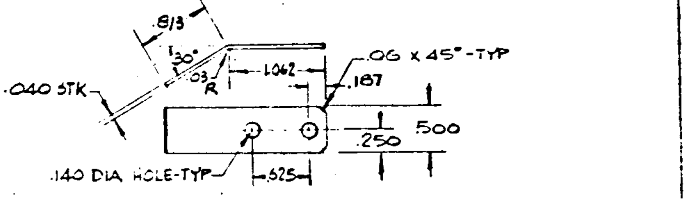
DET -9 MAT'L: TEFLON FINISH: NONE



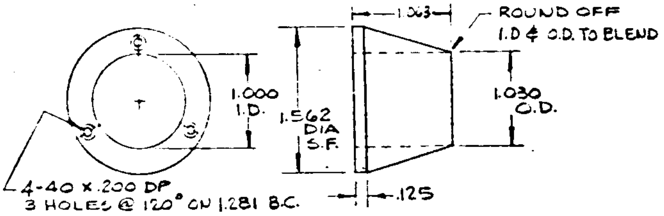
DET -8 MAT'L: C.R.S. FINISH: BLACK OXIDE



DET -7 MAT'L: 50/60 SHORE RUBBER FINISH: NONE



DET -6 MAT'L: BER CU (FULL HARD) FINISH: BLACK OXIDE



DET -5 MAT'L: COPPER (1/2 HARD) FINISH: NONE

ITEM	PART NO.	DESCRIPTION	RE
13		SCREW, 10-32 x 1/2 LG SOC. HD CAP ST'L	14
12		SCREW, 8-32 x 3/8 LG SOC. HD CAP ST'L	2
11		SCREW, 4-40 x 1/4 LG SOC. HD CAP ST'L	5
10		ROLL PIN .093 DIA. X 5/16 LONG	1
9	-9	O-RING SEAL	1
8	-8	DAMPER RETAINER	1
7	-7	DAMPER	1
6	-6	SPRING	1
5	-5	SKIMMER	1
4	-4	PISTON	1
3	-3	SHUTTER	1
2	-2	COVER PLATE	1
1	-1	GUIDE PLATE	1

10-16-66
11-1-66
11/1/66

CHEMATICS RESEARCH
RESEDA CALIFORNIA

VALVE ASSY - HIGH SPEED

001000

SEE DETAILS SEE DETAILS

D 001006

2

APPENDIX

This appendix to Chematics Research Report 4001 has been written in response to the questions raised by JPL concerning the preliminary report submitted as part of the requirements of Contract No. 951573. The questions raised are discussed below.

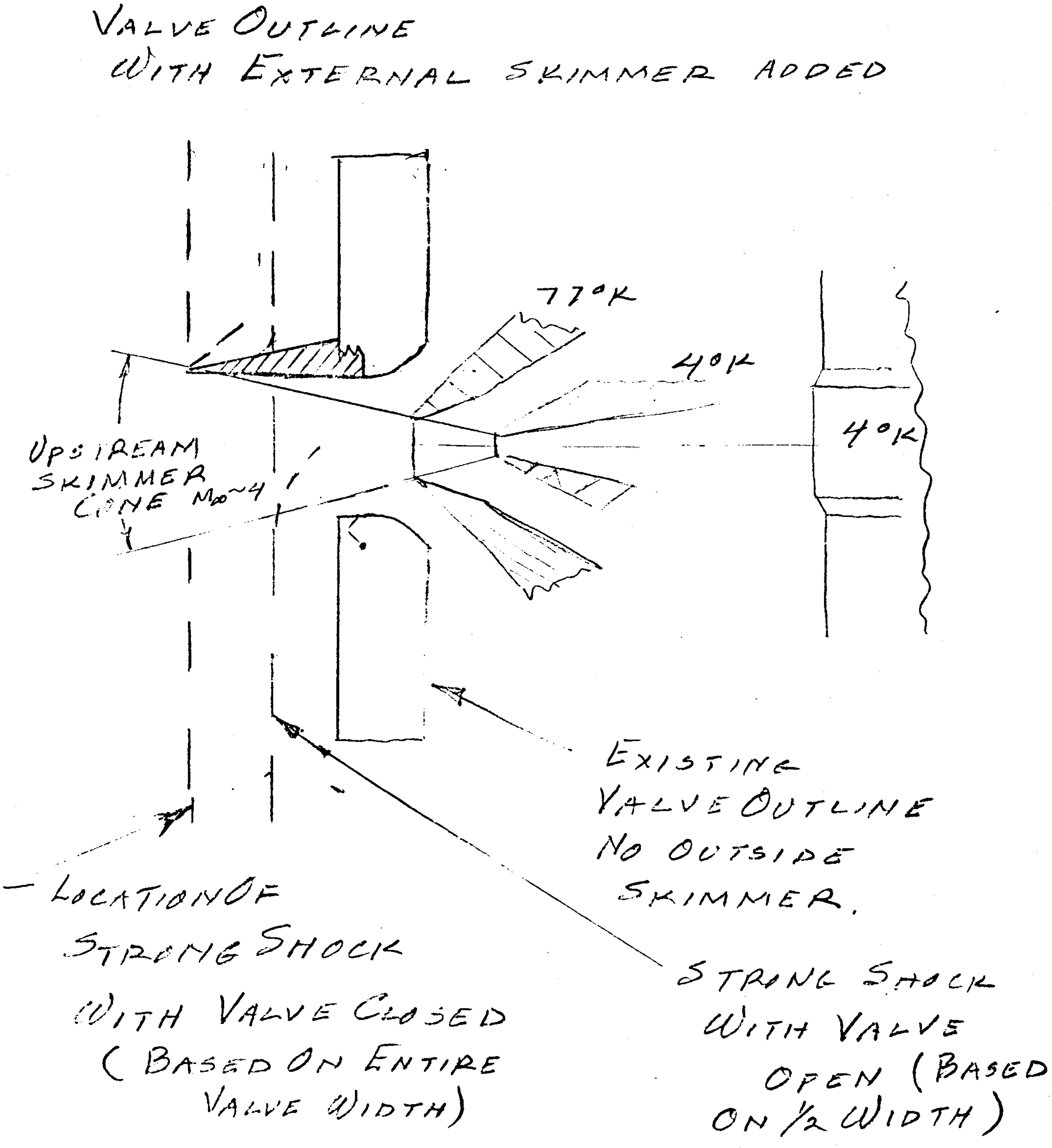
1. Normal Shock Patterns on the Shutter Housing

The first question is probably the most difficult to answer. Shock patterns on blunt bodies are inherently difficult to predict and, in general, are determined experimentally. The following reasoning led to the statement on page 3 of the preliminary report. The sonic line, as shown in Fig. 1A of this appendix, is assumed to be at the corner of the shutter housing so that all the gas flowing through the normal shock must pass through the sonic region. Fig. 1A presents a sketch of the sectional view of the shutter and internal skimmers and indicates the approximate normal shock patterns generated by a Mach 4 or greater flow with both the valve in the open and in the closed position. The shock standoff distance was obtained from the width of the shutter housing, as follows. For a large two dimensional body (i.e., a flat plate) the relative lengths are

$$\frac{y_{max}}{L} \doteq \frac{\rho_s u_s}{\rho_\infty u_\infty}$$

where the length y_{max} is half the body width D, and L is the sonic line length. The subscripts ∞ and s refer to free stream and sonic conditions, respectively, and ρ and u are the local density and velocity.

Figure 1. Sketch of approximate shock location on shutter outline.



The length L is the most important parameter for the shutter assembly since it controls the position of the intruding shock. L can be estimated by rearranging the above and approximating

$$u_s \cong a_s$$

where a_s is the sonic speed behind the shock, so that

$$2L \cong M_\infty D \left(\frac{\rho_\infty}{\rho_s} \right) \left(\frac{a_\infty}{a_s} \right)$$

which gives

$$L \cong 0.25D$$

for Mach 4 flow and

$$L \cong 0.21D$$

for Mach 6 flow. With the external shutter as shown in the preliminary drawings, the statement in the preliminary report is incorrect. The sketch accompanying this appendix (Fig. 1A) indicates that, unless an external skimmer is used to exclude gas processed by the shutter bow shock, disturbances will be felt in the gas sampled. With the shutter mechanism modified as shown in the sketch, only the shock wave generated by the boundary layer on the external skimmer inside diameter will process the test gas. Drawing number 001006 has been modified as indicated on the sketch so that an attached weak shock will exist on the outside of the skimmer. The actual port size should be as large as possible to avoid shock interaction; however, to insure rapid operation, the shutter size should be as small as possible. The existing design is a compromise between these requirements. To insure that the external skimmer does not cause spurious results a tunnel test should eventually be performed.

2. The Vacuum Shaft Seal

The second question concerns the vacuum shaft seal. At least two similar shaft seals have been built and have been reported to be successful. Mamantov, et al., (Rev. Sci. Instr., 37, 836 (1966)) and Thomas ("Fifth International Symposium on Free Radicals, Uppsala", Paper #70, Gordon and Breach, Inc., New York (1961); Trans. Faraday Soc., 57, 1679 (1961); Proc. Roy. Soc., (London), A280, 123 (1964)) have reported successful operation of similar devices at 2500 RPM. The instruments built ny Mamantov and by Thomas were constructed in a relatively casual manner (Mamantov, private communication). Complete engineering drawings were not prepared for either device and the detailed engineering required for concentricity has, apparently, not been necessary for rotational speeds up to 2500 RPM. In designing the present device, a major fraction of the engineering time has been devoted to the details required to obtain successful operation of the seal. Carbonized teflon "O"-rings have been specified and a differential vacuum pumped seal has been included in the design. We feel that the shaft-bearing assembly includes design details totally lacking in either the device of Mamantov or of Thomas. We have especially avoided the problems associated with non-concentricity and, therefore, feel that a high probability for successful vacuum operation exists for the present design.

3. The Squib Operated High Speed Valve

The last engineering question concerns the use of the squib operated valve instead of a capacitor heated wire shutter. A capacitor heated wire shutter is basically a small aperture device so that the use of one in the present application would require that the shutter be located near the cryostat surface. To prevent shocks, the shutter would have to be cryogenically cooled. Finally, an additional slow shutter would be required to seal the external vacuum jacket after completion of the test so that the chemical components could be sampled at a later time. The combination of two shutters and the cooling requirement placed upon the wire shutter finally led to the design of the relatively straightforward squib actuated device. Similar valves are used in gun tunnels and, according to information both from engineers working on such devices and from representatives of the ordnance industry, this unit should operate as predicted.

The entire Chemical Camera has been designed conservatively. The entrance port, shaft seal, and shutter device are all areas where engineering compromises were required. The general cryostat layout was dictated by spatial requirements (*i.e.*, drum size led to nitrogen jacket size, which, in turn, led to the external jacket diameter). The shutter inlet was designed to be as large as possible without severely compromising the probability of successful shutter operation.

4. Analysis of the Record on the Cryostat Drum

The fourth question is concerned with the chemical analysis of the record on the cryostat drum. Classic methods of analysis can be used for the determination of stable and relatively unreactive gases such as CO, CO_2, N_2, and O_2, etc. Gas chromatography, mass spectrometry, and possibly absorption spectroscopy are suitable for such analysis.

Gas chromatography is probably the cheapest and easiest method of analysis of such gases provided proper (low) temperature control and suitable column packings are available. Since retention times provide little *a priori* information about the identity of the components, chromatographs must be calibrated prior to use. Mass spectrometric analysis, however, appears to be more practical for mixtures of the four gases specified. Typical mass spectrometric data for the specified gases are given in Table 1 of this appendix. The exact spectra will, of course, depend upon many factors so that if extreme precision is required, the instrument will have to be calibrated immediately prior to the analysis. However, for most work (and for most spectrometers) the required precision can be obtained with little calibration. Using the intensity at $m/e = 12$, 14, 16, 28, 32, and 44, six equations are obtained in the four unknown concentrations. The overdetermination is desirable partly because of the variability of the 28 peak generated by oxygen on the carbonized tungsten filament. If rhenium filaments are used (common practice in many modern laboratories) this problem is virtually eliminated. However, the overdetermination is still desirable as a check on precision.

If other components are introduced into the mixture, the mass spectrum obtained can generally be interpreted by standard data handling techniques analogous to the procedure described above for the determina-

Table 1

MASS SPECTROMETRIC DATA FOR SELECTED GASES

(70 Volt Acceleration Potential)

Material	m/e	Peak Source°	Intensity	Material	m/e	Peak Source°	Intensity
O_2	16		5.13	CO	12		4.71
	28		3.17*		13	i	0.05
	32		100.00**		14	d	0.75
	33	i	0.08		16		1.67
	34	i	0.41		28		100.00**
	44		0.34*		29	i	1.16
					30	i	0,22
N_2	14		5.18	CO_2	12		6.67
	28		100.00**		13	i	0.09
	29	i	0.73		16		9.40
					28		8.17
					29	i	0.10
					44		100.00**
					45	i	1.12
					46	i	0.39

*Due to reaction with carbonized tungsten filaments. The use of rhenium filaments virtually eliminates these peaks.

**Parent peak

°Peak source: i, isotopic peak; d, doubly charged ion.

tion of oxygen, nitrogen, carbon dioxide, and carbon monoxide mixtures.

Time resolution in the analysis can be obtained by scraping a strip of sample from the cryostat surface and allowing it to warm up on contact with the walls of the apparatus and to expand into the mass spectrometric sampling bulb.

Reactive species, such as free radicals, must be determined by more sopisticated means, as described in the body of this report.

In situ absorption spectroscopy would be difficult in this case primarily because of the spectra of nitrogen and of oxygen. Difficulty could also be expected to arise from the crystallinity of the trapped material.