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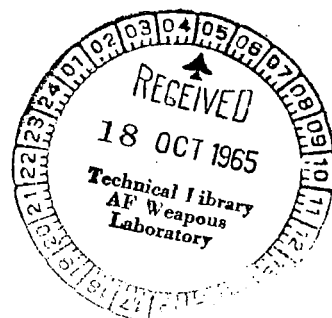NASA CR-314

THE DYNAMICS OF CRYOSORPTION PUMPING

by S. H. Bauer and Peter Jeffers

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • OCTOBER 1965

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ABSTRACT

A technique has been developed for the rapid injection of gas samples into a low pressure system (Knudsen regime), and for faithfully recording the consequent changes in pressure. The experimental procedure may be used for measurement of initial rates of adsorption on a millisecond time scale, and in this investigation was used for dynamically testing the speed of cryosorption pumping of air, argon and hydrogen by activated charcoal (temperature: liquid nitrogen). The utility of cryosorption pumping has been demonstrated for the rapid removal of bursts of gas as well as for obtaining and holding pressures down to $10^{-6} - 10^{-7}$ mm. Hg. The initial pumping rate is limited by a "geometric" sticking coefficient, which depends on the gas. After about 10 milliseconds the pumping rate declines and appears to be limited by the rate of diffusion of molecules into the cracks and pores of the large area adsorbent.

INTRODUCTION

Dynamic measurements were made of the speed of pumping by activated charcoal cooled to liquid nitrogen temperature. This study was undertaken to evaluate cryosorption for three applications. The first, as a means of rapidly removing the gas injected as a burst in dump tanks which comprise the transition section from a shock tube to the ion source of a time-of-flight mass spectrometer. The second application is the development of a very rapid pump to maintain a local low pressure within an electron diffraction apparatus during the injection of gaseous samples. The third is the maintainance of pressures in the 10^{-7} mm range in the arc chamber of an analytical mass spectrometer during continued arcing.

To make these measurements it was necessary to devise methods for rapid gas injection in the Knudsen flow regime, and for following rapid pressure changes at sub-micron levels. For the former we used a miniature shock tube, and for the latter a dc operated ionization gauge and a dual trace oscilloscope for recording concurrently the total electron emission and the positive ion current.

APPARATUS AND PROCEDURE

Pittsburgh Activated Carbon Co. charcoal types BPL 12x30 and FCB 12x30 were tested, with Celanese water base emulsion polymer CL-303 as a binder. Although zeolite would have proved equally effective, and merits investigation, for our application charcoal is preferred since the latter releases adsorbed water when warmed to room temperature so that no additional heating is essential. The supporting surface was a 2" x 11" x 1/16" sheet of copper, bent into a spiral. Serpentine copper tubing (1/8" I.D.) was soldered to the strip to provide direct cooling by the liquid nitrogen. The CL-303 binder was diluted so that it consisted of 10% solids, and was then mixed 1/1, proportioned by weight, with activated charcoal. The paste was rapidly applied to the pumping panel to a thickness of about 3 mm. Forty grams of charcoal were thus spread onto the panel, which was cured at 120°C for two hours. The geometric area (charcoal covered and liquid nitrogen cooled) is approximately 140 cm^2; the estimated surface area is 4×10^4 m^2. In this study we did not ascertain the possible loss in surface area of the charcoal due to local covering by the emulsion polymer.

The tests were made with the arrangement sketched in Figure 1. The ion gauge was an NRC type 507 (glass mantle cut off); slowly varying pressures were read with a control circuit, NRC Equipment Corp. type 710B. For the measurement of rapid changes the battery powered circuit shown in Figure 2 was used; oscilloscope deflections were calibrated against the NRC control. The pressure response was found to be linear in the region of interest. It proved essential to record concurrently the grid current and the positive
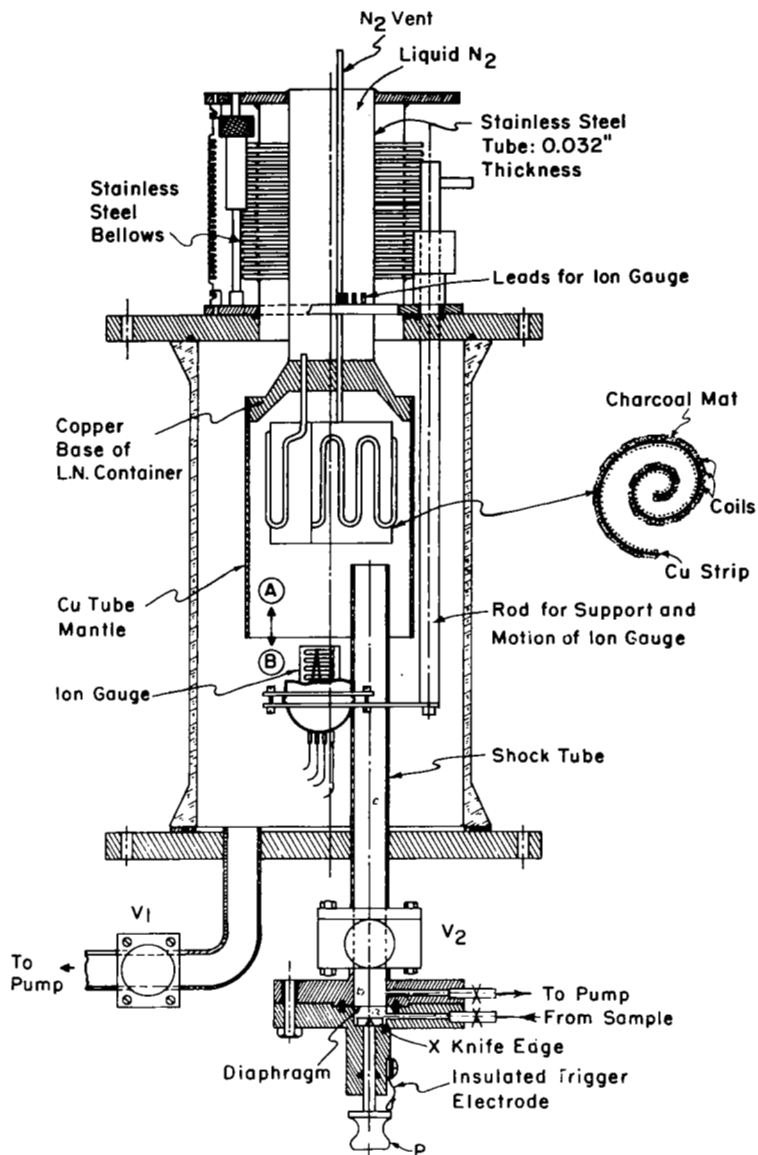
Figure 1. Apparatus for testing cryo-pumping rate

The bellows and spiral strip support was designed for insertion above the injection nozzle in an electron diffraction apparatus. The bellows and 3 spacing screws are needed to permit accurate positioning of the CU tube mantle with respect to the electron beam. The mantle also serves as a radiation shield.

For rapid gas injection region (a) is filled with sample to a pressure between 0.1 and 38 cm Hg. With valve V_2 open, regions (b) and (c) are at the low pressure of the large vessel. The diaphragm is burst by hitting plunger P. V_2 is closed for replacing the diaphragm and recharging the "high pressure" chamber.

ion current since the magnitude of the latter is directly proportional to the product of the molecular density and the electron flux. The filament emission was found to change appreciably during a gas burst. The power supplies in the NRC control unit are not adequately filtered, and the circuit contains a feedback loop which regulates the emission, but response to regulations is limited to 60 cps, which is too slow for the tests described.

Diaphragms for the "shock tube" were of cellophane. The plunger was in the shape of a pointed "X", 2 cm. diameter; the diaphragms were cut cleanly into 7 or 8 radial petals. The high pressure chamber had a volume of 5 ml and was filled to pressures which ranged from 1 mm to 38 cm Hg. Since expansion to 6.2 liters occurred, the final expected pressures (for no pumping) ranged from 10^{-1} to 10^{-3} mm Hg. The ion gauge was supported on a solid sliding rod and could be placed within the copper tube mantle which enclosed the charcoal coated pumping surface (the top of the ion collector was within 2 cm of the bottom of the spiral; position A), or it could be situated 15 cm from the copper spiral (position B), as indicated on Figure 1.

RESULTS

With the system newly assembled and valve V_1 open to the diffusion pump and the charcoal at room temperature, the ion gauge read 2×10^{-4} mm. On closing V_1 a leak rate of 0.3 microns/minute was observed. When liquid nitrogen was poured into the container the pressure fell to 2×10^{-6} mm in 20 minutes (V_1 closed) and was steady for several hours. A small leak was found and repaired; this reduced the leak rate to 0.1 micron/minute. Upon cooling the panel from room temperature with liquid nitrogen the pressure fell from 1×10^{-4} to 5.6×10^{-6} mm in four minutes, and to 4×10^{-7} mm in 20 minutes. The lowest observed pressure (V_1 closed) was 1.4×10^{-7} mm, and could be held for up to 4 hours.

Preliminary tests with rapid gas injection were made using the NRC control circuit. These tests indicated that the gas was being injected and adsorbed very rapidly. In fact, the response time of the meter was the limiting factor. The observed maximum deflections of the meter needle suggested that the ionization gauge was sensing less than 25% of the injected air: the rest was adsorbed during the response time of the instrument.

Figure 3 shows typical oscilloscope traces recorded with the battery powered circuit. The top and bottom straight lines are the zeros for grid and plate currents, respectively. The vertical amplifiers were set so that 1 division represents a pressure of 9×10^{-5} mm Hg, while 1.35 division equals 5 milliamp grid current. The finite rise time noted on the pressure trace is limited by the opening time of the diaphragm and the rate of flow of the injected gas through tube c and the test vessel. The ion current traces were corrected for changes in electron emission, and reduced to pressure curves such as shown in Figure 4. Note the
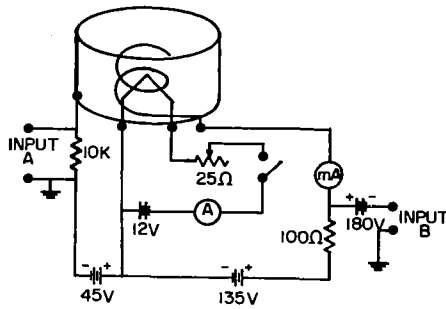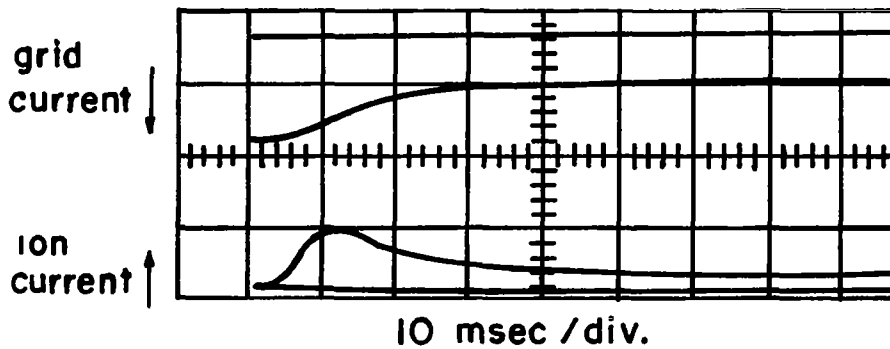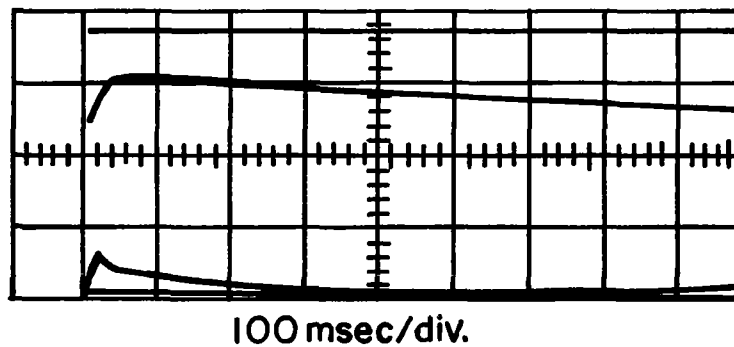
Figure 2.

Circuit for ion gauge, for the measurement of rapid pressure changes. A Tektronix 535 oscilloscope with type CA dual trace plug-in unit was used.

grid current ↓

ion current ↑

10 msec /div.

a) Injection of 1 mm. air onto BPL charcoal. Lower trace is of the ion current and the upper trace is of the grid current. Sweep speed 10 msec/division.

100 msec/div.

b) 0.5 mm injected under conditions similar to (3a). Time scale 100 msec/div. Grid current returned slowly to its initial level after most of the injected gas had been removed.

Figure 3.

difference between the pressures recorded with the gauge inside and outside the copper mantle. These typical differences are limited to the first 10 milliseconds and imply that a significant amount of cryopumping takes place during the time required for the gas to spread from the point of injection throughout the vessel. To ascertain the efficiency of pumping for large bursts, a sample of air at 38 cm Hg was injected; the initial pressure was 7×10^{-7} mm. Although the expected pressure for no pumping was 0.31 mm, the pressures observed in 10 seconds, 5 minutes, and 15 minutes were 3×10^{-4}, 2×10^{-5}, and 6×10^{-6} mm. The injected air would give a monolayer coverage of about 9.8 m^2. Since the charcoal is quoted as having a surface area of 1100 m^2/gram, the apparently efficient handling of a comparatively large volume is to be expected. Additional results are summarized in Table I.

ANALYSIS OF THE DATA

No attempt was made to develop a quantitative theory for the observed pressure patterns; clearly it will prove difficult to formulate equations for the finite gas flow rates at these low pressures in a complex geometry. Nevertheless a semi-quantitative analysis led to interesting conclusions. The instantaneous injection rate was assumed to depend on the moles of gas (m_i) which remained in the driver section (a):

(1)
$$\frac{dm_i}{dt} = \beta(m_o - m_i) = m_o \beta e^{-\beta t}$$

β is a constant characteristic of the gas and the geometry of the broken diaphragm, which proved to be unexpectedly reproducible. The pumping rate was assumed to be the kinetic theory collision rate, based on the geometric area (A) of the pumping panel, and an accomodation coefficient (α):

(2)
$$\frac{dm_p}{dt} = \frac{\alpha}{4} \frac{A\bar{c}}{RT} p(t) \quad ; \quad$$

$\bar{c}$ mean molecular speed

p(t)   instantaneous pressure within the copper mantle.

The net change in pressure follows the equation:

(3)
$$dp/dt + \gamma p = \xi e^{-\beta t}$$

$$\gamma = \frac{\alpha A}{4V} \bar{c} \quad ; \quad \xi = p_o V_o \beta/V$$

p_o, V_o are the pressure and volume, respectively, of the high pressure chamber (a) of the shock tube, and V is the volume of the complete system. This equation is
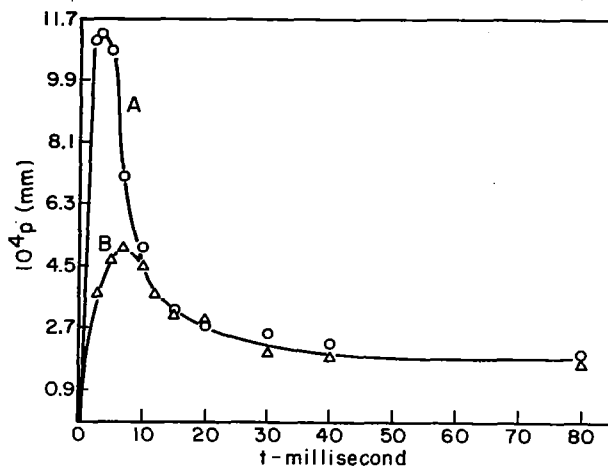
Figure 4.

Ion current traces corrected for electron emission. 1.5 mm air was injected into an initial pressure of 7×10^{-7} mm. For no pumping the expected pressure was 1.25×10^{-3} mm. Curves A and B refer to the ion gauge position, inside and outside of the copper mantle, respectively.
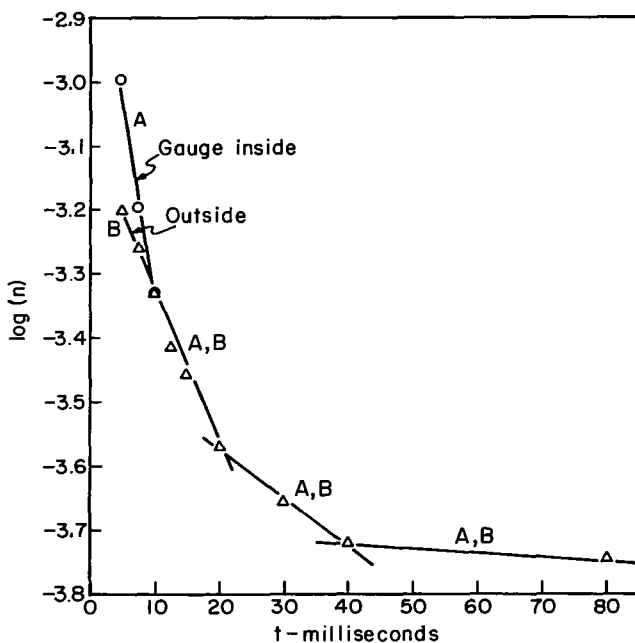

Figure 5.

Log n vs t for injection of 1.5 mm. air onto FCB charcoal (pressure data given in Fig. 4 for gauge positions A and B). Discrete linear portions were drawn to emphasize the inferred presence of different stages in the redistribution process.

TABLE I

Sample ($V_o = 5$ cm^3)	P(initial)	P(no pumping)	P$_{max}$(obs)	P(final)	Type of carbon
2 mm air	1×10^{-6}	1.7×10^{-3}	6.6×10^{-4}	4×10^{-5} (80 msec)	F C B
1 mm H$_2$	3.5×10^{-7}	8.3×10^{-4}	8.3×10^{-4}	7×10^{-7} (2 min.)	F C B
2 mm Ar	9×10^{-7}	1.7×10^{-3}	9.9×10^{-4}	6.8×10^{-5} (80 msec)	F C B
2 mm air	6×10^{-7}	1.7×10^{-3}	5.4×10^{-4}	1×10^{-6} (15 sec)	B P L
2 mm air	2×10^{-6}	1.7×10^{-3}	7.2×10^{-4}	3×10^{-6} (15 sec)	B P L
1 cm air	7×10^{-7}	8.3×10^{-3}	1.4×10^{-3}	6×10^{-6} (15 sec)	B P L
10 cm air	6×10^{-6}	8.3×10^{-2}	8.2×10^{-3}	6×10^{-5} (15 sec) 1×10^{-5} (3 min)	B P L
19 cm air	7×10^{-6}	1.6×10^{-1}	1.4×10^{-2}	2×10^{-4} (15 sec) 2×10^{-5} (3 min)	B P L
3.5 mm Ar	6×10^{-7}	3×10^{-3}	2.7×10^{-3}	3×10^{-6} (15 sec)	B P L

TABLE II

Injection	t_{max} (sec)	γ	α initial
1.5 mm air, gauge inside.	0.003	135	0.51
1.5 mm air, gauge outside.	0.007	40	0.15
2 mm air, gauge outside.	0.0065	50	0.19
3.5 mm Ar, gauge outside F C B CARBON[a]	0.010	10	0.045
1 mm H$_2$ F C B CARBON[a]	0.016	0.1	10^{-4}

(a)   FCB activated carbon is impregnated with iron and copper oxides for removing hydrogen by chemisorption at liquid nitrogen temperatures.

readily solved provided neither α nor $\bar{c}$ are functions of the time.

$$(4) \qquad p(t) = \frac{p_o V_o}{V} (1 - \gamma/\beta)^{-1} \exp(-\gamma t) [1 - e^{-(\beta-\gamma)t}]$$

Recordings of the pressure transients for the case of no cooling gave the following values for β (deduced from the time required to reach 0.9 of the final pressure); air and argon, $\beta \approx 355$ sec^{-1}; hydrogen, $\beta \approx 570$ sec^{-1}. These relative magnitudes are expected from the corresponding sound speeds at room temperature. Values of γ and hence of α were then deduced from the time at the peak pressures, recorded when the panel was cooled.

$$t_{max} = (\beta-\gamma)^{-1} \ln (\beta/\gamma)$$

Typical magnitudes are listed in Table II. Past the maximum, for $t > 2/(\beta-\gamma)$, it follows from Eq. 4 that the moles adsorbed (n) are logarithmically dependent on the time; the slope of a plot of $\log_{10} n$ vs t should be $\frac{\alpha}{2.303} \cdot \frac{\bar{c}A}{4V}$. Figure 5 is such a replot of the pressure curves shown in Figure 4. Since A/V is a constant, the different regimes to which attention is directed by the straight line portions, indicate several regimes in $(\alpha\bar{c})$. Due to cooling of the injected gas from room temperature to about 77°K by collision with the cryo-panel, $\bar{c} = (8RT/\pi M)^{1/2}$ should decrease with time. But the maximum expected decline is $(77/300)^{1/2} \approx 0.5$, whereas the product $(\alpha\bar{c})$ changed by a much larger factor. These experiments therefore demonstrate that α decreases with the amount of gas adsorbed.

At the first break (15 msec) the amount of gas adsorbed corresponds to monolayer coverage of the geometric area of the cryopumping panel. However, the total gas injected was insufficient to cover the available area with a monolayer. Hence, we conclude that the high initial pumping rate was limited by diffusion of the initially adsorbed gas molecules to the internal adsorption sites. From these measurements it appears that the time required for statistical redistribution onto the total available surface is of the order of a minute. (It may be of the order of seconds, but this could not be established without extensive revision of the experimental arrangement). Thereafter, a second injection, without allowing the panel to warm up, produces the same pressure-time pattern.

SELECTED REFERENCES ON CRYO-PUMPING

1. N. M. Kuluva and E. L. Knuth, "Sorption Pumping at Pressures Less Than 10^{-5} TORR", Amer. Vacuum Soc., Trans. Ninth Sym., 1962, pp. 237-242.

2. M. Manes and R. J. Grant, "Calculation Methods for the Design of Regenerative Cryosorption Pumping Systems", Amer. Vacuum Soc., Trans. Tenth Sym., 1963, pp. 122-127.

3. L. O. Mullen and M. J. Hiza, "Some Cryogenic Applications in The Production of High and Ultra-High Vacuum". Preprint 45A, Sym. Molecular Prop. at Cryogenic Temps., 56th AICHE Meeting, 1963.

4. L. O. Mullen and R. B. Jacobs, "Some Characteristics of a Simple Cryopump". Amer. Vacuum Soc., Trans. Ninth Sym., 1962, pp. 220-226.

5. D. W. Breck, J. Chem. Ed., 41, 678 (1964) - - - on zeolite