



Technical Note

73

**SOME EXPERIMENTS ON
THE DEPOSITION OF
GASES AT 4.2° K**



**U. S. DEPARTMENT OF COMMERCE
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OCTOBER 1960

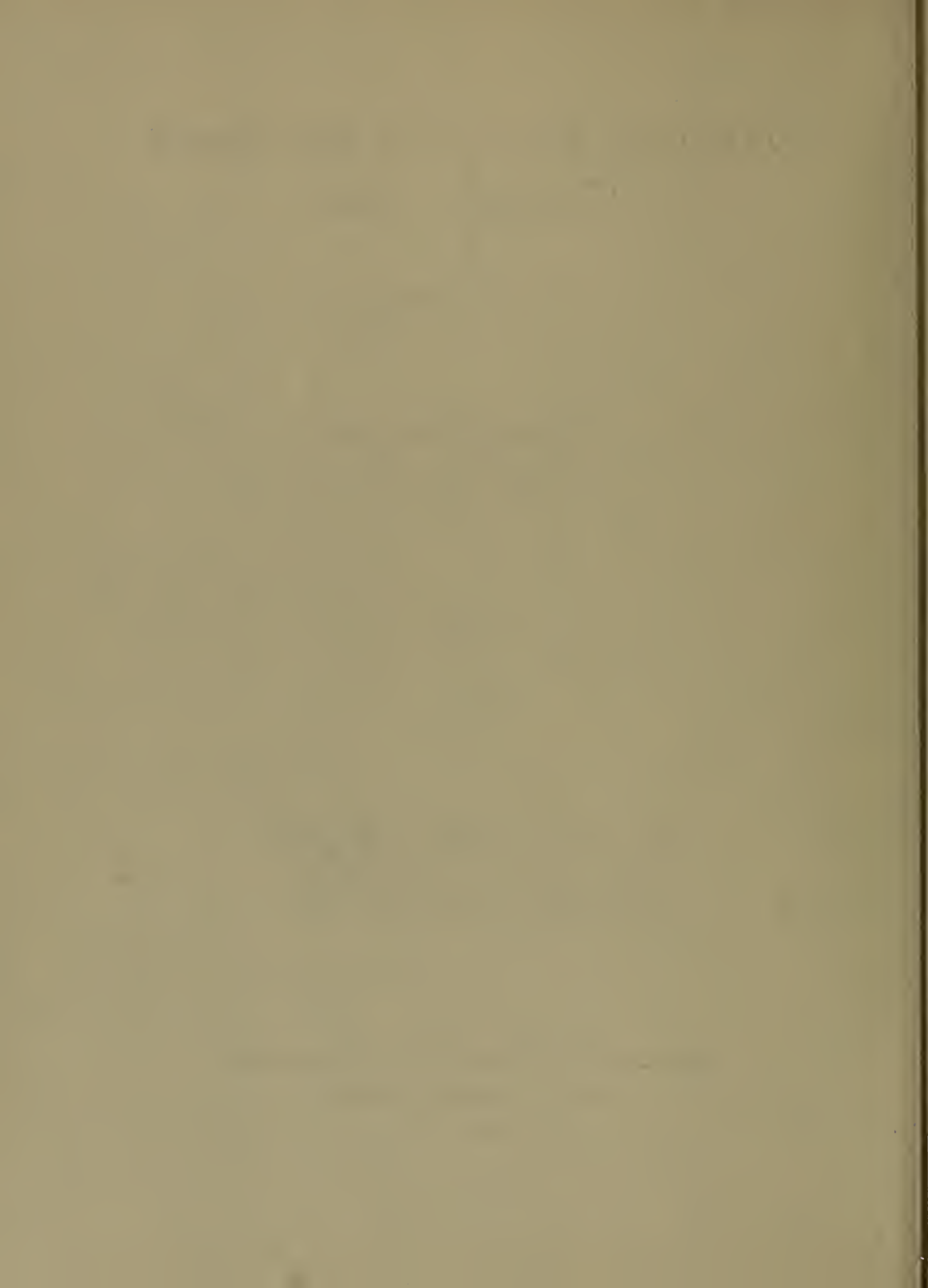
SOME EXPERIMENTS ON THE DEPOSITION OF GASES AT 4.2° K

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Some Experiments on the Deposition of Gases at 4.2 °K * †

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In order to develop some preliminary information concerning the very basic problems of gaseous deposition at extremely low temperatures, samples of argon, nitrogen, oxygen, and hydrogen were deposited at 4.2 °K, and variations in some of the parameters associated with these depositions were observed. In addition, samples of the same gases were passed through an excitation zone prior to deposition, and differences in the deposition behavior were recorded. The pressure downstream of the deposition region and the temperature within the deposited solids were found, in general, to increase with flow rate of the depositing substances, and to vary with time in a manner depending on the density, flow rate, and state of excitation of the incoming gases. Arrhenius curves were plotted using warm-up data observed in these experiments and solid-phase transition data determined elsewhere. Variations in the positions of these plots were sometimes the result of differences in the conditions of deposition, and at other times an effect of the chemical nature of the gas studied. The experimental behavior of hydrogen, relative to that of the other gases studied, was observed to be strongly dependent upon its much higher thermal conductivity.

INTRODUCTION

The method of Broida and Pellam [1] for trapping energetic species at or below liquid helium temperatures has been used

* This research was performed under the National Bureau of Standards Free Radicals Research Program supported by the Department of the Army.

† Presented before the 138th national meeting of the American Chemical Society, New York City, September 1960.

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extensively, both in the experimental program on the nature of free radicals at the National Bureau of Standards [2] and in related programs elsewhere [3]. However, those who have worked with this method have often been handicapped in the interpretation of their experimental results by a lack of fundamental knowledge as to the detailed nature of gaseous deposition at low temperatures.

The necessity has been recognized for obtaining experimental data and developing theories relevant to the following aspects of the problem: (a) flow parameters for gases moving toward cold surfaces; (b) mass, energy, and momentum interactions associated with collisions between gases and cold surfaces; (c) modes of crystal growth of deposits at extremely low temperatures; (d) surface mobilities of newly deposited species as a function of matrix composition; (e) the tendency of deposited species to escape back to the gas phase during continuing deposition; (f) chemical interactions at or on cold surfaces; (g) mechanisms of distribution and absorption of energy within and through the solid deposits; and (h) effects of all these factors upon the physical and chemical changes occurring as the deposited materials are revaporized during warm-up.

A complete set of answers to these basic problems cannot be immediately forthcoming. In the present work we have investigated some of these aspects in order to provide preliminary information concerning the broad area of gaseous deposition at extremely low temperatures.

APPARATUS

The gases used in this work, viz., high-purity argon, nitrogen, oxygen, and hydrogen, were deposited both in their ground states and in a mixture of excited states produced by passage through a microwave (2450 Mc) electrodeless discharge zone.

The basic deposition vessel, shown in figure 1, was the heart of the vacuum apparatus used in this work. As can be seen, this vessel consisted of a group of four coaxial tubes. The outermost of these provided the deposition surface and enclosed the system. The innermost tube acted as a gas inlet route. Gases were drawn directly from their cylinders through Tygon tubing to dry ice-acetone traps and thence through flowmeters to a gas inlet manifold and the deposition vessel. The flowmeter tubes were used more to provide a measure of constancy of flow than to meter the flow, inasmuch as the gases flowed

at tank pressures, with no attempt being made to adjust to atmospheric pressure. The manner of measuring actual flow rate will be described below.

The two intermediate tubes within the deposition vessel were connected at their lower ends and formed a warming jacket, the inside of which was open to the atmosphere or to circulating dry nitrogen at room temperature. The use of this jacket prevented precooling of the incoming gas prior to its impingement upon the deposition surface at the bottom of the outermost tube. An additional thin tube was suspended from a ring-seal at the jacket inlet stopcock and hung freely within the jacket walls. This provided a means for bringing in the dry nitrogen for warming the jacket, and insured good circulation through the jacket.

The annulus between the innermost tube and the jacket provided, by suitable arrangement of the gas inlet manifold, an additional gas inlet when desired. On the other hand, the annulus between the warming jacket and the outermost tube led to a dead end. This region, as seen in figure 1, was downstream from the deposition surface, with respect to the incoming gas. Pressure in this downstream region could be monitored during deposition. During a run, therefore, the only means of removing incoming gases was the cold surface; there was no other pump in that part of the system once the downstream portion was closed off.

The inside of the innermost tube was coated with General Electric Dri-Film (R) 88, a mixture of silicones. The purpose of this coating was to minimize the wall-catalyzed recombination of dissociated gases, especially hydrogen, which had been passed through the microwave discharge zone. Wittke and Dicke [4] have reported a similar treatment, and justified its use solely on the basis of "crude quantitative tests" of its wall-poisoning effectiveness as compared with that of several other treatments (p. 625, op. cit.). The effectiveness of the treatment used in the present work was not tested at all, it being assumed that the silicone coating obtained was at least as effective as that of Wittke and Dicke.

Two copper-constantan thermocouples were incorporated into the construction of the deposition vessel. One of these was sealed through the bottom of the outermost tube of the deposition vessel, and was made to lie on the deposition surface in such a way as to measure temperatures within the deposited solids. The other was placed in the end of the innermost tube to provide a measure of the constancy of incoming gas temperature

prior to deposition. Flow of dry nitrogen through the warming jacket could usually be so adjusted as to maintain this temperature to within 5% of 240 °K. Calibration of the thermocouples was carried out in liquid helium, hydrogen, and nitrogen, and was in agreement with calibrations of similar thermocouples, as carried out by Dr. Norman L. Brown of the National Bureau of Standards Free Radicals Research Program, who extrapolated his values to a curve drawn to correspond in shape to curves taken from Southard and Andrews [5] and from Aston, Willihnganz, and Messerly [6]. The uncertainty in thermocouple readings was always ± 1 microvolt, which corresponded to approximately ± 0.65 °, 0.15 °, 0.06 °, and 0.05 °K at the boiling points of helium, hydrogen, nitrogen, and oxygen, respectively.

Immediately below the deposition vessel was a double dewar containing liquid helium with liquid-nitrogen and double-vacuum jacketing. It could be raised to surround the deposition vessel, or it could be lowered away from the vessel, by a manually-operated jack, so as to provide refrigerant at any desired level. By suitable manipulation of the liquid helium level at varying distances below the deposition surface, temperature at the glass could be regulated to within about 5% of any desired value.

Above the deposition vessel and mounted around the gas inlet tubes leading to it were waveguides connected to two microwave generators. These provided microwave electrodeless discharges at 2450 Mc and a maximum of 125 watts, for exciting and dissociating incoming gases, when desired.

Pressure in the downstream region of the deposition apparatus was measured by a Pirani gage and by a cold cathode ionization gage. A second Pirani gage was located in the upstream portion of the innermost gas inlet tube. Elsewhere in the system, an ordinary mercury manometer was available for measuring over-all system pressure, and a McLeod gage was available for calibration. For all pressure measurements in the refrigerated part of the system, thermal transpiration corrections were made whenever the measured pressure was less than 65 microns Hg, the various gages themselves being always at room temperature.

The deposition vessel was connected through a gas inlet manifold of rather complex design and through a main manifold to the main pumping system. Finally, a portion of the system designed for measuring total volume of gases deposited consisted of the manometer mentioned above, a known volume (871 cc), and a Toepler pump.

PROCEDURE

In a typical run, the gas flowed into the system past one of the waveguides and through the cylindrical gas inlet route. It was then condensed on the circular surface at the bottom of the deposition vessel. The level of liquid helium in physical contact with the vessel was maintained as closely as possible in the plane of the deposition surface. The only exception to this rule was in the case of hydrogen, for which the helium level always had to be held somewhat higher, in approximately the plane of the end of the jacket. Downstream pressure and the temperature in the deposit were observed regularly, sometimes at minute-by-minute intervals, throughout the deposition. In addition, upstream pressure and the temperature of the incoming gas stream were monitored and the liquid helium level was adjusted whenever necessary. The deposit could be observed at all times through an unsilvered vertical strip in the helium dewar.

Upon the termination of deposition, the inflowing gases were cut off and the helium level was usually brought up high enough on the deposition vessel to immerse the entire glass section containing the solids deposited. Gas circulation in the warming jacket was stopped, and the jacket was evacuated by rough-pumping. The decays of downstream pressure and deposit temperature were usually followed after gas cut-off until they had reached equilibrium levels.

The condensate was then allowed to begin warming. This was accomplished either by mechanically lowering the helium dewar, or by allowing the liquid helium level to drop slowly below the deposition surface, as the helium boiled off. Measurements of pressure over and temperature within the deposit were made as the warm-up proceeded. If enough liquid helium still remained when warm-up had proceeded to some temperature slightly below the normal boiling point, the deposition surface was again immersed in refrigerant, and the gas redeposited and revaporized for as many cycles as possible.

Finally, the total amount of gas originally deposited was permitted to flow to the gas measurement section of the apparatus. This was usually done piecemeal, the last bits of significant volume increments being cycled through the Toepler pump. After each volume of gas was measured, it was pumped out of the system. The true flow rate of the depositing gas was then determined from the total volume thus measured, as reduced to standard conditions, integrated over the total time of deposition.

RESULTS

The variations of downstream pressure and deposit temperature with time and flow rate during the depositions of both ground-state (undischarged) and excited (discharged) argon, nitrogen, oxygen, and hydrogen are charted in figures 2-12. The measured parameters generally increased for all four gases as functions of flow rate. They also increased for nitrogen and oxygen as functions of excitation regardless of flow rate.

In addition, the downstream pressure increased with time for argon, excited argon, nitrogen, oxygen, and excited oxygen at constant high flow rates (greater than 50 standard cc/min); the same parameter decreased with time for oxygen and hydrogen at lower flow rates; and it tended to be invariant with time for argon, excited argon, and nitrogen at and below 50 standard cc/min, and for hydrogen and excited hydrogen at high flow rates. The variation of pressure with time for excited nitrogen was erratic.

The geometrical form of the various deposits ranged from truncated cones, the radius of the truncation corresponding approximately to the radius of the gas inlet tube, to disk-shaped solids. The tendency to cone formation usually increased for greater amounts of total material deposited. Because of these variations in form, it proved impossible to determine any consistent value of thermal conductivity of any of the solids. In the case of hydrogen, a rather fluffy solid was laid down on the deposition surface and also on the nearby vertical surfaces. All deposits were white, except for the well-known blue-green color associated with excited nitrogen [7].

For gases admitted to the system (at 17-152 standard cc/min) through the cylindrical inlet tube, the observed upstream pressures were compared with Poiseuille pipe-flow calculations. The observed values in every instance deviated from calculated values by a factor no greater than two in either direction.

Figures 13-15 are the warm-up curves for ground-state (undischarged) and excited (discharged) argon, nitrogen, and oxygen, respectively. The corresponding curves for hydrogen are not shown, since these warm-up data were inconsistent. The curves of figures 13-15 were drawn as a series of straight lines, and the pertinent data are summarized, with appropriate annotations, in Table I. It may not appear from these graphs that the curves always correspond to the experimental points as closely as might be desired. This is because the straight lines were based only partially on the experimental points shown; additional data used

in plotting these lines were the known transition phenomena summarized in the last column of Table I [8].

Considering the curves as drawn, some differences appeared in the warm-up data for first vaporizations as opposed to later vaporizations, and for the discharged gases as opposed to the ground-state gases. These differences will be discussed below.

Certain effects associated with the warm-ups may be cited here. In the case of discharged nitrogen, for example, the characteristic glows described and spectroscopically analyzed in many papers of Broida and his co-workers [9] were observed. In addition, the single run with discharged oxygen was terminated by an explosion which was attributed to the presence of ozone in the solids deposited [10]. This explosion occurred when the pressure in the system had reached about 400 mm Hg, during the gas-transfer and volume-measurement phase of the run. As a result, the flow rate in this instance had to be estimated from the available data.

DISCUSSION

It was noted above that in general, both downstream pressure and temperature of the solid during deposition increased as functions of the flow rate of any given incoming gas. This manner of variation was probably a result of increasing amounts of heat released at the condensation surface as increasing amounts of gas were deposited, per unit time.

In a similar fashion, the increases observed for the same two variables as functions of the excitation of nitrogen and oxygen indicated significant increases in the energy released on condensation of the excited species when compared with the respective ground-state molecules. The same effect was not as marked, and may not even have occurred, for argon. This probably reflected a higher degree of reversibility of the modes of energy absorption for gaseous nitrogen or oxygen than for argon flowing through the same energy discharge zone at comparable molar flow rates. That is, argon was capable of more efficiently storing its excitation energy in the solid phase than the other gases, a conclusion which is further substantiated below. The observed results for hydrogen were marginal, and may have been masked by thermal conductivity effects which are discussed more fully below.

Where any variation of downstream pressure with respect to time of condensation was observed under given conditions of gas composition, excitation, and flow rate, this was probably the

principal effect of a slower approach to dynamic equilibrium in the particular system studied than in other systems where downstream pressure was relatively constant with time. The generalized trend of such variations was that the downstream pressure tended to: (a) decrease with time for low-density gases at low flow rate; (b) increase with time for high-density gases at high flow rate, or for high-density gases passed through the discharge zone; and (c) remain invariant with time for intermediate cases.

Behavioral differences between hydrogen and the other gases studied manifested themselves in several respects, as may be seen by comparing the data of figures 10-12 with those of figures 2-9. For one thing, it was noted earlier that in order to obtain hydrogen deposits at all, the liquid helium level had to be kept higher on the deposition vessel than for the other three gases studied. Any time the liquid helium level was allowed to drop appreciably, the rate of hydrogen deposition dropped sharply, as evidenced by surging downstream pressure in the system. Also, it was not possible, as in the other cases, to prevent precooling of incoming hydrogen by the use of the warming jacket filled with flowing nitrogen at room temperature; great quantities of nitrogen quickly condensed to liquid in the jacket, and measured temperature of the inflowing hydrogen dropped to 77 °K or slightly below. This probably was partially responsible for the greater and more consistent deviations of the observed head pressure, e.g. 58-78%, from values predicted by the Poiseuille calculations for flowing hydrogen than for the other gases.

Again, whereas downstream pressures in depositing argon, nitrogen, and oxygen were usually of the order of 10^{-4} to 10^{-7} mm Hg depending on the flow rate, they were observed to be much higher, e.g. 10^{-1} to 10^{-4} mm Hg, for hydrogen at comparable flow rates. Thus hydrogen exhibited much lower probabilities of sticking, under the conditions of this work, than the other gases. Finally, it has already been pointed out that the behavior of the hydrogen deposits on warm-up was so erratic as to lead to wholly inconsistent data which could not be plotted with any degree of reliability.

The effects described above are qualitatively understandable, however, when we take into account that these are basically thermal transport phenomena which have been observed, and that the thermal conductivity of gaseous hydrogen is anywhere from six to eight times that of the other three gases studied. Thus, it would be expected that hydrogen would behave differently and be harder to handle, as was the case.

In an effort to evaluate the deposition data in terms of some unifying principle, an attempt was made to correlate these data with the predictions of a simple theoretical model* derived from considerations of thermal balance in the deposit. The assumption was made here that the measured downstream pressure might be considered as a measure of temperature at the surface of the deposit, as opposed to the observed deposit temperature which was taken from the interior of the solids. The results of calculations based on this model were inconsistent and totally inconclusive. It is believed that the negative results of this phase of the work were due to nonequilibrium effects in the deposit, as for example, heat generation accompanying crystalline rearrangement during the deposition. Thus, the model could not be applied to these experiments.

The available warm-up data have been summarized in figures 13-15 and Table I. As noted above, no consistent warm-up data were obtained for hydrogen, so this discussion will be confined to considerations affecting only argon, nitrogen, and oxygen. Several features relating to these data are worthy of comment at this point.

It will be noted, first of all, that the warm-up curves for any one gas underwent a shift on going from the unexcited to the excited case. For argon (fig. 13), this shift (from portions B,C,D to E,F,G) was in the direction of higher pressure at any given temperature for the excited gas. This reflects a greater release of energy in the form of additional amounts of vaporizing species at any given temperature, when the argon had been energized in the discharge prior to its original deposition.

A similar effect was noted in nitrogen (fig. 14), except that the extent of the shift (from portions C,D,E to G,H,J) may not have been very significant when the scatter of points in these regions is taken into account.

In the case of oxygen (fig. 15), the observed shift was in the opposite direction for the excited gas, i.e., to lower pressure at any given temperature. Again in this instance the extent of the shift (from portion C to D) may not have been significant. It could be argued that since the amount of ozone vaporizing from the

*For this model, I am indebted to Dr. Sidney Golden of Brandeis University, consultant to the National Bureau of Standards Free Radicals Research Program.

condensate had to be two moles for every three moles of oxygen originally reacting ($3O_2 \rightarrow 2O_3$), a sufficient quantity of ozone storage in the condensate of excited oxygen could explain such a shift in the vapor pressure curve as is shown in figure 15. However, it would be very difficult to prove that this actually happened in this work.

Let it be supposed that the shifts noted in the nitrogen and oxygen vapor pressure curves were indeed of minor significance, and that the vaporization of excited species from these condensates released approximately the same amounts of energy as the vaporization of the respective ground-state molecules, while the extent of the energy shift from ground-state to excited argon deposits on vaporization was somewhat more substantial. Under this assumption, comparison of these results with the observed variations in the deposition parameters for the various ground-state and excited gases leads to the conclusion that energy storage was more efficient in the case of the argon deposits than for nitrogen or oxygen, where greater amounts of energy were released in the course of the original condensation. The case of hydrogen is, as stated earlier, marginal or inconclusive on the evidence of these experiments, but would be expected to parallel the case of the other diatomic gases. The greater amounts of energy release on condensation of the diatomic gases is probably a direct effect of recombination mechanisms in these gases as they impinge on the respective deposits. Such mechanisms do not, of course, come into consideration in the deexcitation of argon.

In addition, portions of the warm-up curves for both ground-state and excited argon, and for excited oxygen, may be seen in figures 13 and 15 to have shifted in one direction or another with varying degrees of significance, in going from the first vaporization of the respective deposits to later vaporizations of the redeposited materials. In the case of ground-state argon (fig. 13), the shifts from portions C,D to C',D' indicate lower energy releases at temperatures below 35 °K for later vaporizations than for the first vaporization. This may reflect a greater degree of ordering in the crystalline argon during the relatively rapid redepositions of this gas than during the slower first deposition. This effect is particularly significant over portions D and D', i.e., at temperatures less than about 10 °K, and may not truly exist between 10 ° and 35 °K, i.e., over portions C and C'. In excited argon, on the other hand (fig. 13), the marginally significant shift from portion G to G' is in the direction of greater energy release on later vaporizations, at temperatures below 10 °K, indicating the possible loss by the solid phase of additional increments of the

original discharge energy upon revaporization of the same material.

In figure 15, a shift is observed on going from the first to subsequent vaporizations of excited oxygen (containing ozone). This shift, from portions B,D to F,E appears to be anomalous unless we again argue the storage of large quantities of ozone in the deposit, and postulate further that the ratio of gaseous ozone to oxygen was higher during later warm-ups than on the first vaporization. We do know that ozone was present because of the explosion mentioned earlier and the references cited in [10]. We also know that portion E of figure 15 is the only case of a warm-up curve with a negative slope as observed and plotted, i.e., a negative heat of sublimation as shown in Table I-C. The reasons for this are not clear, but might also relate to the release of ozone in the later warm-ups on a scale which had not been realized in the first vaporization. However, it should be pointed out at this point that portions F and E were derived from only one run, number 303, which because of the explosion which terminated it was never repeated. We therefore know nothing about the reproducibility of these portions, except that junction FE does correspond to a known physical phenomenon (cf. Table I-C).

Finally, portion F of the nitrogen warm-up curves in figure 14 marks a phase which, as noted in Table I-B, exists only for nitrogen deposited at low flow rates. In the particular run in which the points determining this part of the curve were recorded (no. 201), the flow rate was 17 standard cc/min. No runs were carried out with excited nitrogen at any comparably low flow rate.

CONCLUSIONS

The following conclusions have been drawn from this work:

1. In the condensation of gases at extremely low temperatures, the amount of heat released at the cold surface varies directly as the volume flow rate of the depositing species. Corresponding increases occur in such parameters as the pressure in a closed volume downstream of the deposit and the temperature within the deposit.

2. In such condensations, the downstream pressure tends to: (a) decrease with time for low-density gases at low flow rate; (b) increase with time for high-density gases at high flow rate, or for high-density gases subjected to excitation before

deposition; and (c) remain invariant with time for intermediate cases. Where the extremes of time variation are observed, the flowing system may be considered to undergo a slower approach to dynamic equilibrium than is true of the time-independent cases.

3. Upon warm-up of the solids described in this study, sufficient regularity of pressure and temperature variation is attainable in all cases except hydrogen, so that Arrhenius plots may be drawn which are reasonably consistent with solid-phase transition data determined elsewhere.

4. The available evidence indicates that monatomic gases subjected to excitation prior to deposition are capable of storing greater quantities of their excitation energy in the solid phase than diatomic gases similarly treated. In the latter case, it appears that recombination of dissociated molecules prior to or coincidental with condensation leads to the loss of significant amounts of excitation energy from the condensate. These considerations may be modified in the case of excited oxygen because of the formation of ozone.

5. During warm-up of deposited gases, some shifting of the Arrhenius plots may occur as a result of repeated deposition-vaporization cycles with the same gas sample. The reasons for these shifts may be tentatively assigned to energy effects within the solids deposited. This effect appears to be particularly significant for ground-state argon at temperatures below 10 °K.

6. The behavior of gases in such deposition-vaporization cycles as were carried out in this work is much more erratic and difficult to control for gases of relatively high thermal conductivity, as illustrated by the case of hydrogen.

These experimental data and conclusions have provided information which we hope will lead to a fuller understanding of gaseous deposition at very low temperatures. It is yet too early to formulate a theory consistent with all the known facts regarding this phenomenon.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Drs. Herbert P. Broida and Arnold M. Bass, who were respectively Chief and Assistant Chief of the N.B.S. Free Radicals Research Section when this work was done, and to many other members of the Section for

much help and encouragement. To Mr. Alfred K. Stober, thanks are especially due for much valuable aid and many suggestions relating to the experimental set-up and procedures.

Dr. Miriam Sidran of Grumman Aircraft Engineering Corporation rendered invaluable assistance in rewriting and editing this paper from its original form as a National Bureau of Standards report.

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Table I. Summary of Warm-up Data

A. Argon (fig. 13)

Letter Indices for:		Temp. or Range (°K)	Pressure or Range (mm Hg)	Associated Phenomena and Comments	
<u>Vapor Curves</u>	<u>Break Points</u>			<u>Heat of Sublimation (cal/mole)*</u>	<u>Nature of Transition [8]</u>
Ground-State:					
A		> 66.7	> 30	1860	(See Notation, fig. 13)
	AB	66.7	30		Appearance of Liquid Phase
B		66.7-33.3	30-0.0016	1300	
	BC	35.7	0.0045		Annealing
	BC'	33.3	0.0016		Annealing
C		35.7-12.1	0.0045 to 1.27x10 ⁻⁶	297	
C'		33.3- 9.3	0.0016 to 1.80x10 ⁻⁸	292	
	CD	12.1	1.27x10 ⁻⁶		Recorded Transition
	C'D'	9.3	1.80x10 ⁻⁸		Recorded Transition
D		< 12.1	< 1.27x10 ⁻⁶	35.4	
D'		< 9.3	< 1.80x10 ⁻⁸	34.9	
Excited:					
	AE	66.7	30		Appearance of Liquid Phase
E		66.7-36.4	30 - 0.6	623	
	EF	36.4	0.6		Annealing
F		36.4- 9.6	0.6 to 4.0x10 ⁻⁶	309	
	FG	9.6	4.0x10 ⁻⁶		Recorded Transition
	FG'	10.3	1.28x10 ⁻⁵		Recorded Transition
G		< 9.6	< 4.0x10 ⁻⁶	32.9	
G'		< 10.3	< 1.28x10 ⁻⁵	34.5	

*From Arrhenius calculations.

Table I (Continued).

B. Nitrogen (fig. 14)

Letter Indices for:		Temp. or Range (°K)	Pressure or Range (mm Hg)	Associated Phenomena and Comments	
Vapor Curves	Break Points			Heat of Sublimation (cal/mole)*	Nature of Transition [8]
Ground-State:					
A		> 59.0	> 49	1670	(See Notation, fig. 14)
	AB	59.0	49		Appearance of Liquid Phase
B		59.0-35.6	49-0.37	867	
	BC	35.6	0.37		Phase Change
C		35.6-31.0	0.37-0.25	187	
	CD	31.0	0.25		Secondary Change, Restricted Rotation, Possible Vapor Pressure Effect.
D		31.0-22.5	0.25 to 2.5×10^{-4}	1130	
	DE	22.5	2.5×10^{-4}		Annealing
E		22.5-12.6	2.5×10^{-4} to 2.8×10^{-6}	256	
	EF	12.6	2.8×10^{-6}		Transition at Low Flow Rates of Deposition only.
F		< 12.6	< 2.8×10^{-6}	18.0	
Excited:					
	BG	35.6	0.37		Phase Change
G		35.6-31.0	0.37-0.275	141	
	GH	31.0	0.275		Secondary Change as for CD (above)
H		31.0-22.5	0.275 to 0.0027	754	
	HJ	22.5	0.0027		Annealing
J		< 22.5	< 0.0027	303	

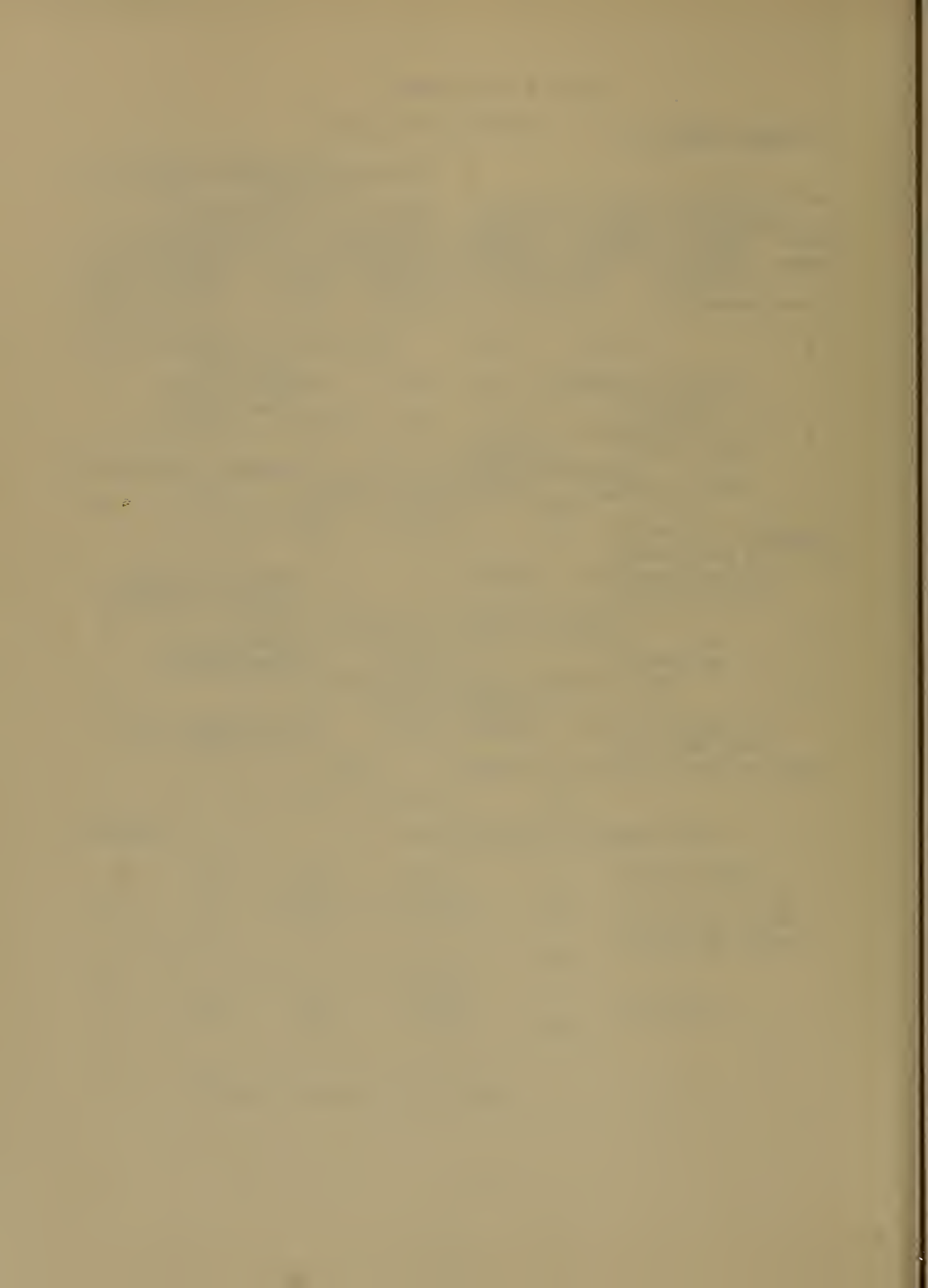
*From Arrhenius calculations.

Table I (Concluded).

C. Oxygen (fig. 15)

Letter Indices for:		Temp. or Range (°K)	Pressure or Range (mm Hg)	Associated Phenomena and Comments	
<u>Vapor Curves</u>	<u>Break Points</u>			<u>Heat of Sublimation (cal/mole)*</u>	<u>Nature of Transition [8]</u>
Ground-State:					
A		> 59.0	> 6.0	1760	(See Notation, fig. 15)
	AB	59.0	6.0		Appearance of Liquid Phase
B		59.0-25.0	6.0 to 2.9×10^{-4}	855	
	BC	28.6	0.00185		Ordering (Annealing?)
C		< 28.6	< 0.00185	258	
Excited:					
	BD	25.0	2.9×10^{-4}		Transition from Glass to β -Crystal
D		< 25.0	< 2.9×10^{-4}	246	
	AF	59.0	6.0		Appearance of Liquid Phase
F		59.0-25.0	6.0 to 4.7×10^{-6}	1210	
	FE	25.0	4.7×10^{-6}		Transition as in BD (above)
E		< 25.0	> 4.7×10^{-6}	- 82.8	

*From Arrhenius calculations.



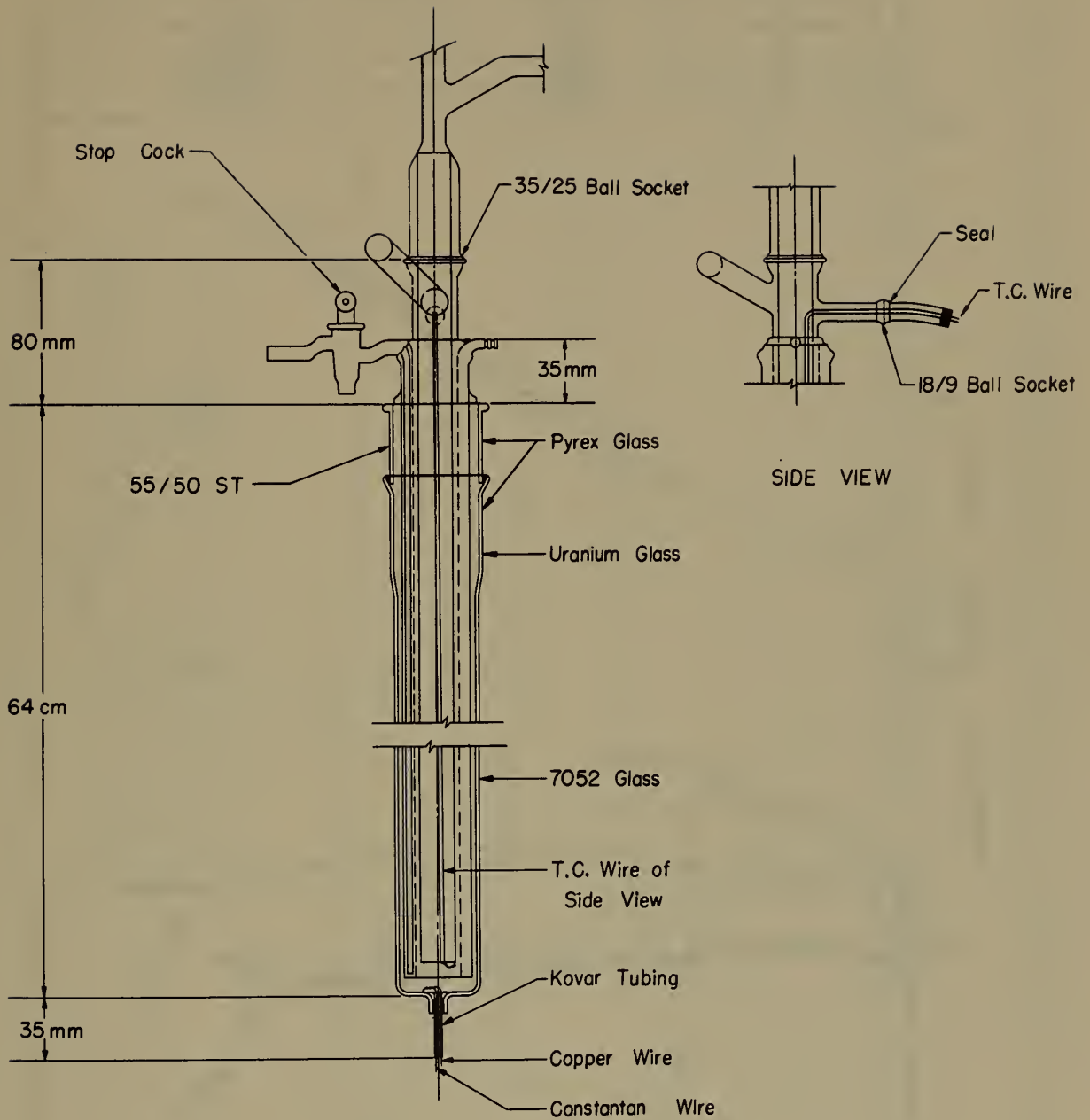


Figure 1. The deposition vessel.

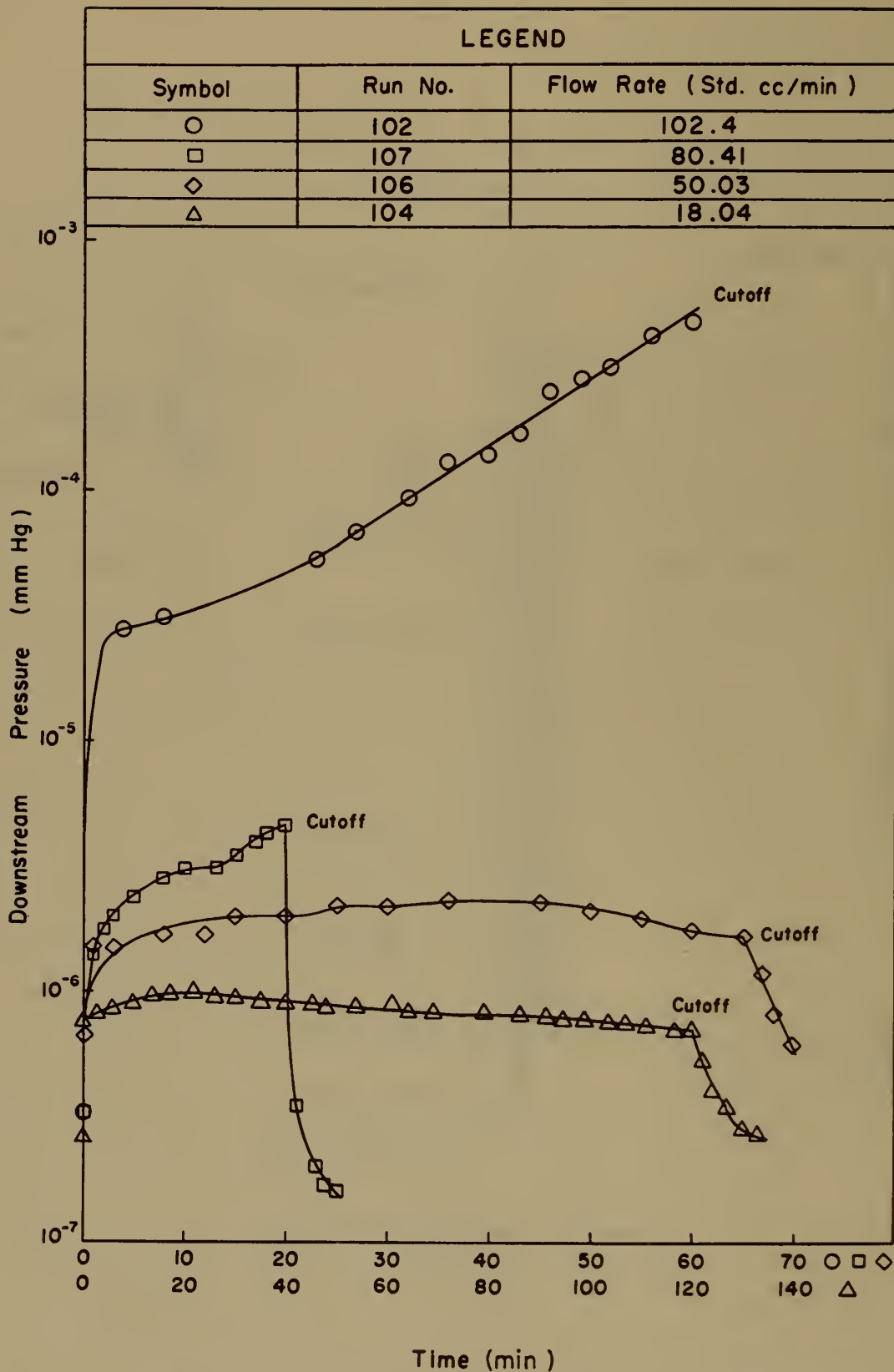


Figure 2. Variation of downstream pressure during deposition of ground-state argon.

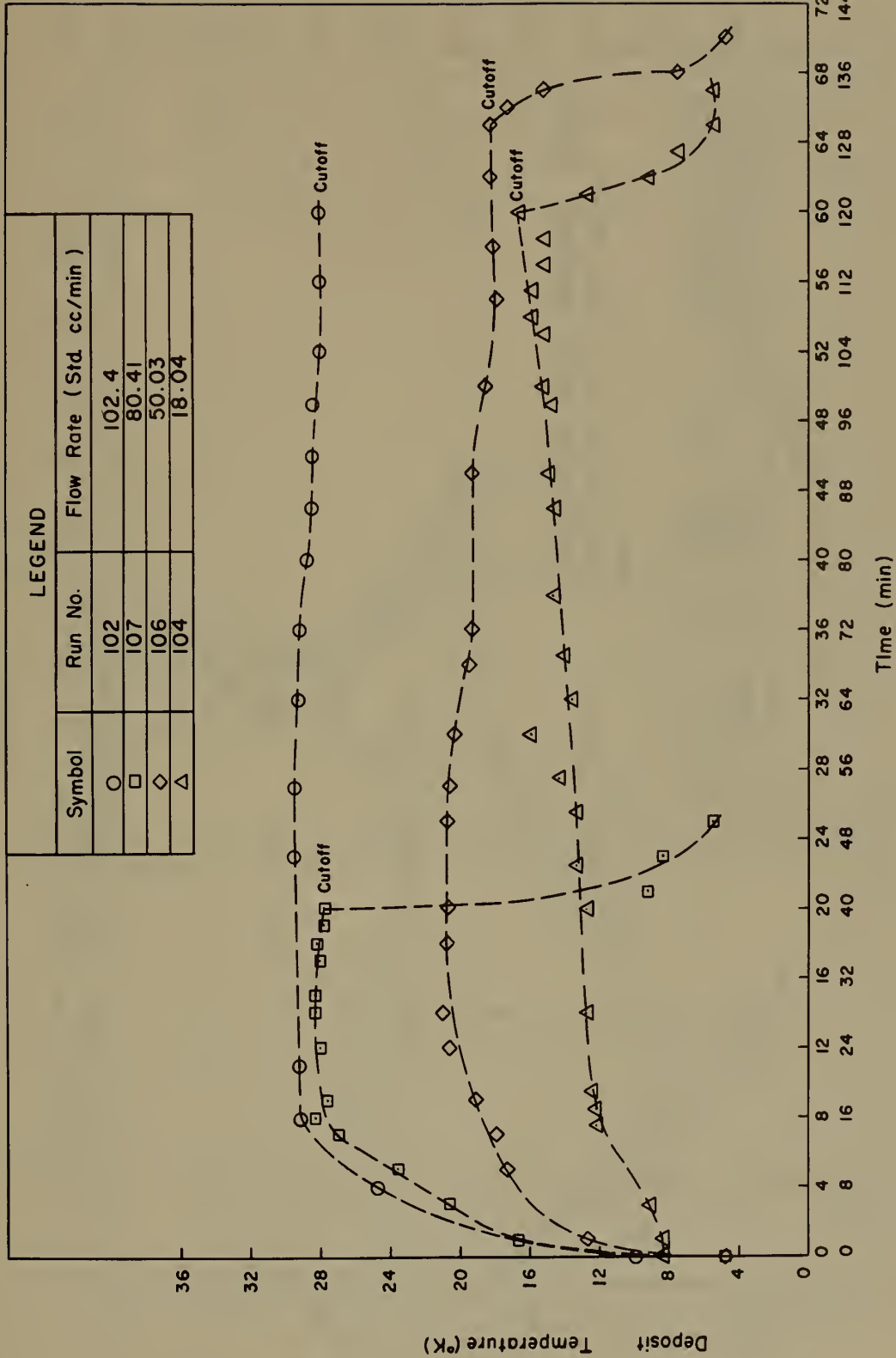


Figure 3. Variation of deposit temperature during deposition of ground-state argon.

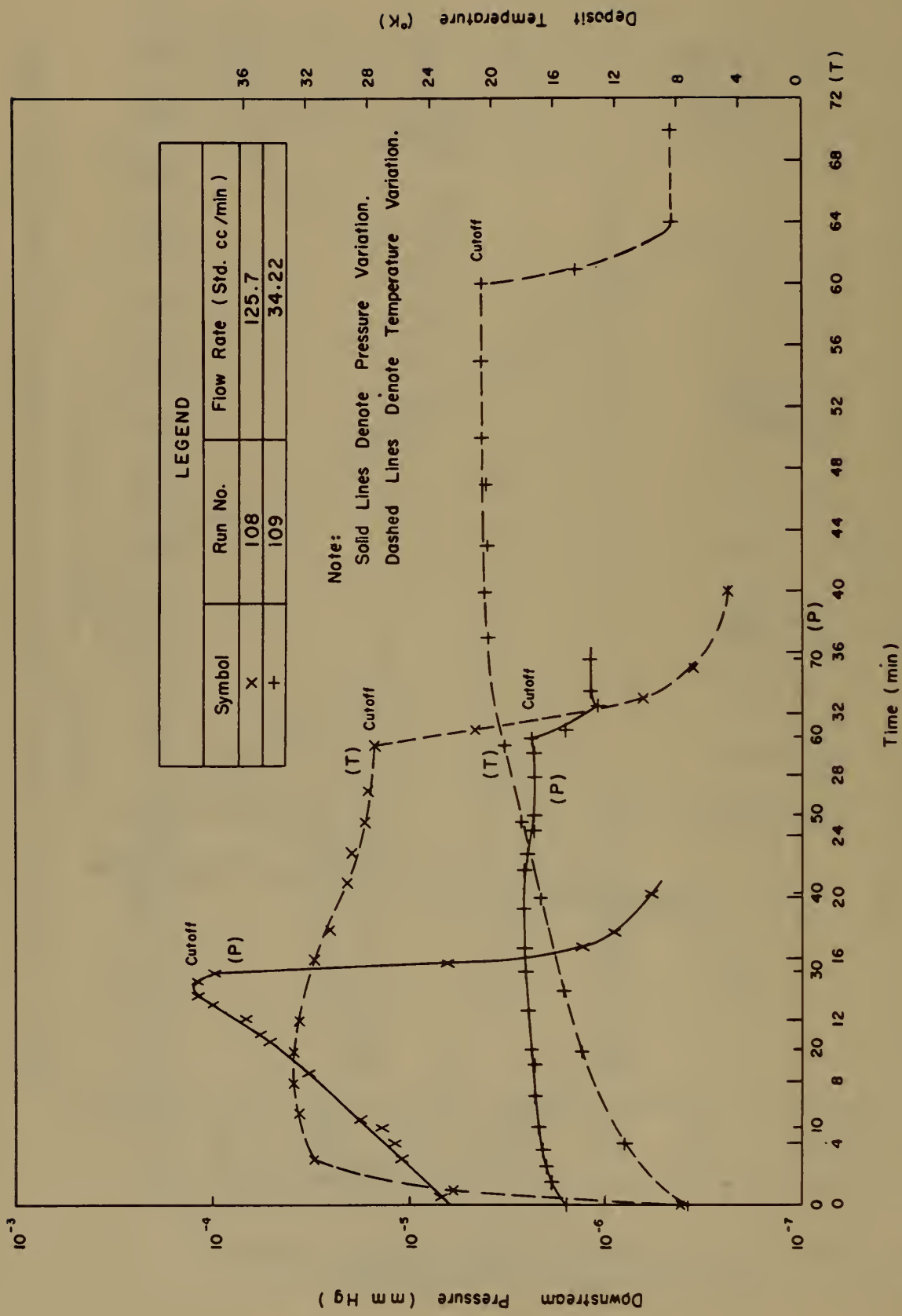


Figure 4. Variation of downstream pressure and deposit temperature during deposition of excited argon.

LEGEND

Symbol	Run No.	Flow Rate (Std. cc /min)
○	202	75.88
□	204	55.96
◇	201	16.87

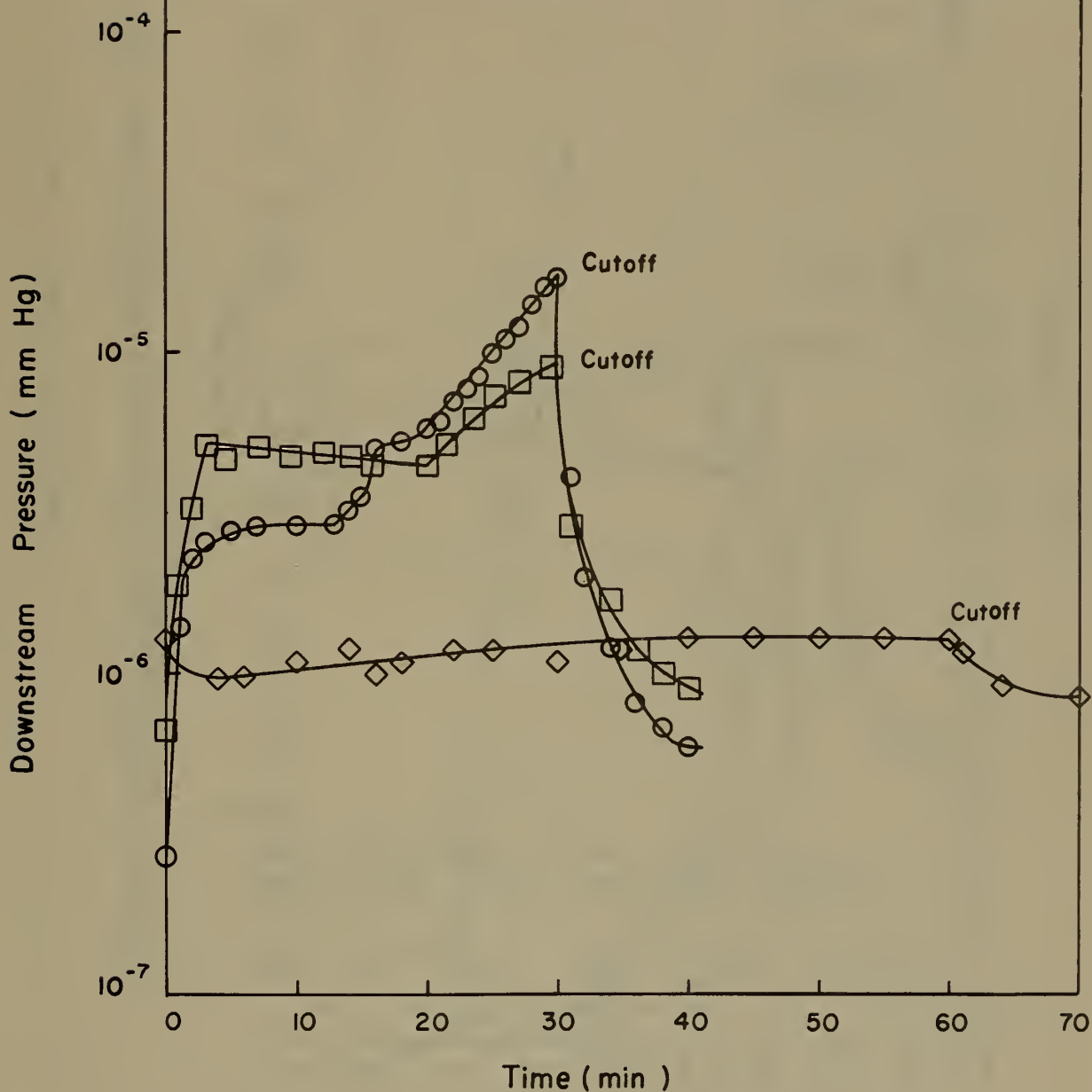


Figure 5. Variation of downstream pressure during deposition of ground-state nitrogen.

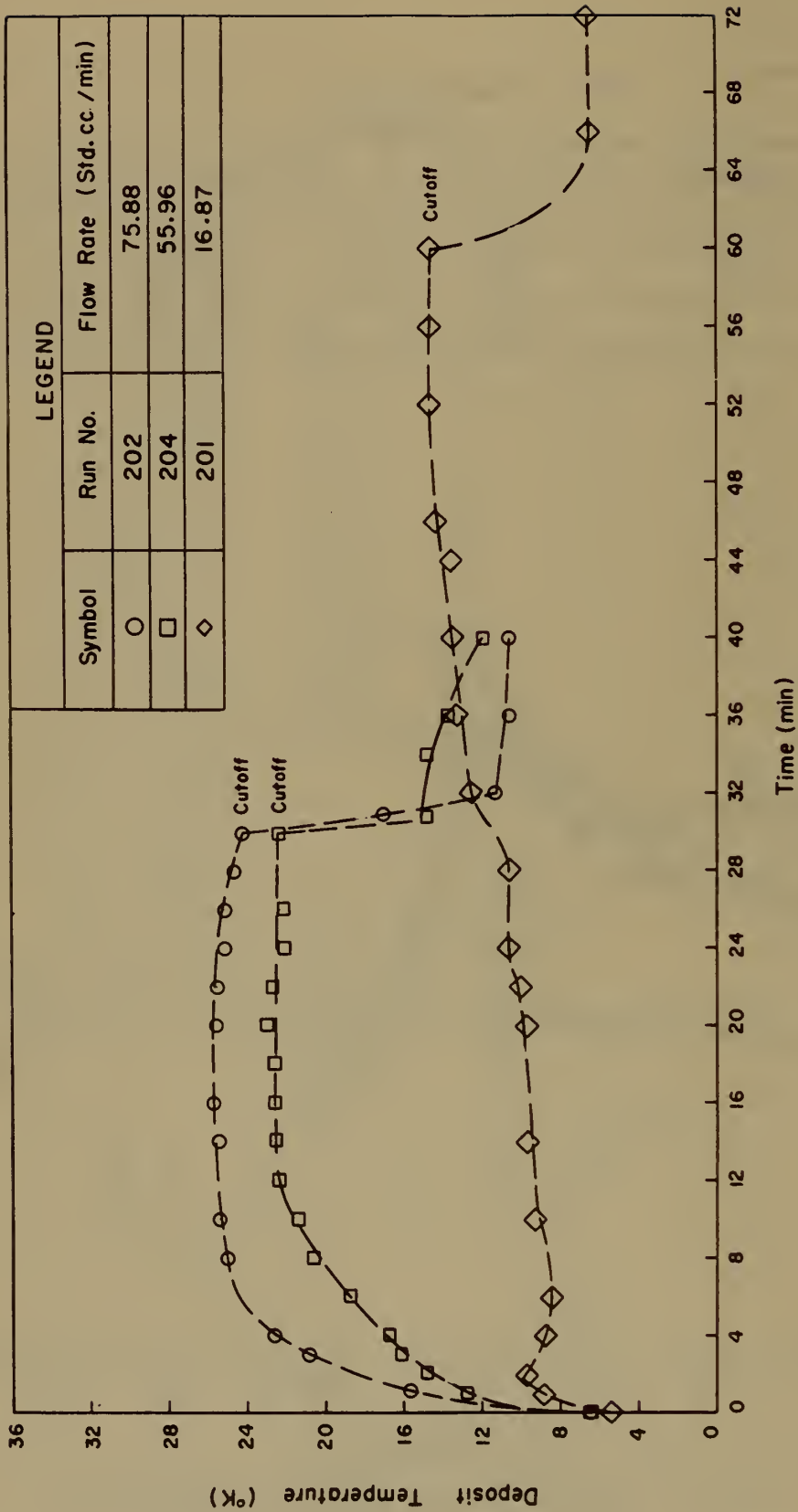


Figure 6. Variation of deposit temperature during deposition of ground-state nitrogen.

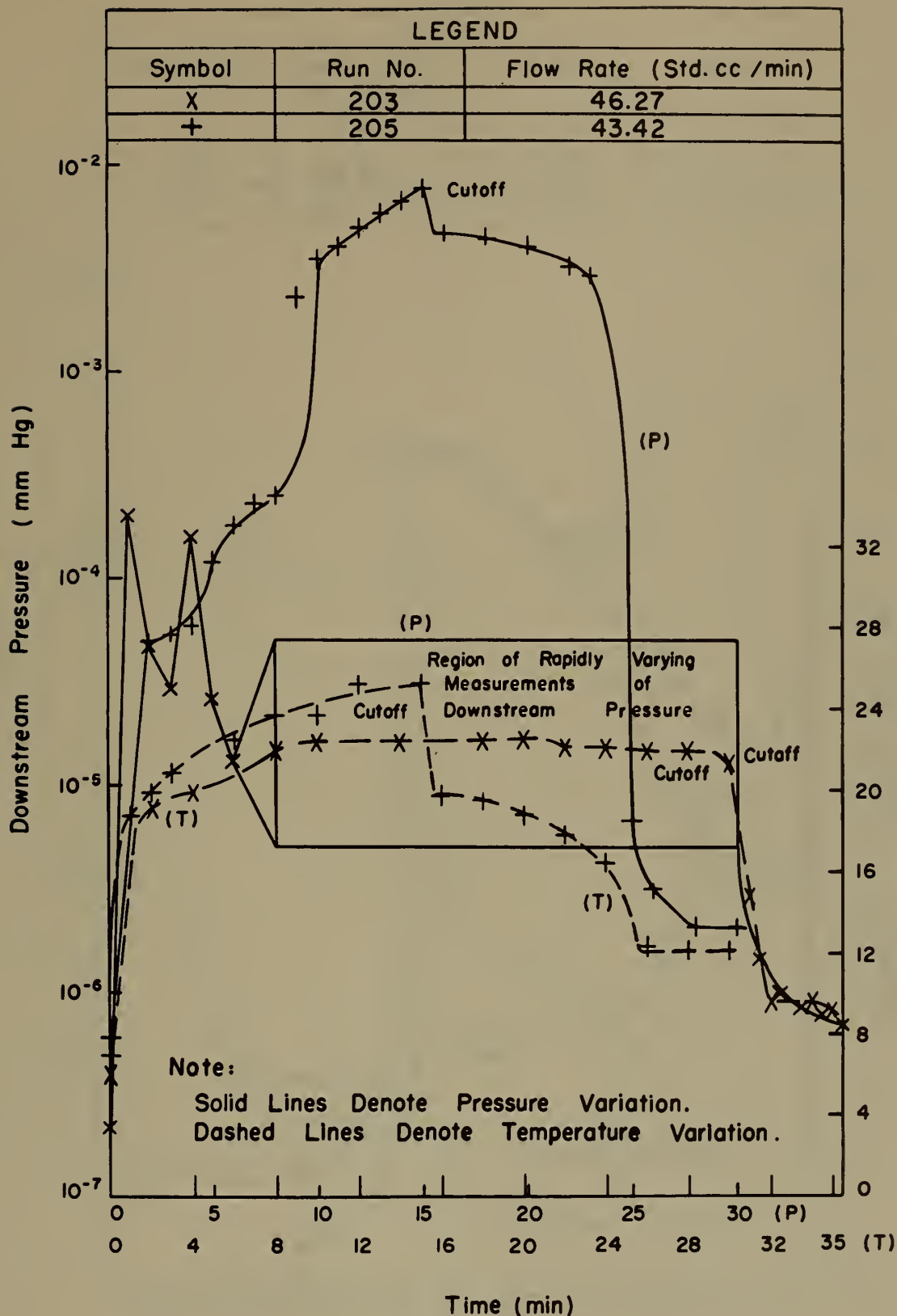


Figure 7. Variation of downstream pressure and deposit temperature during deposition of excited nitrogen.

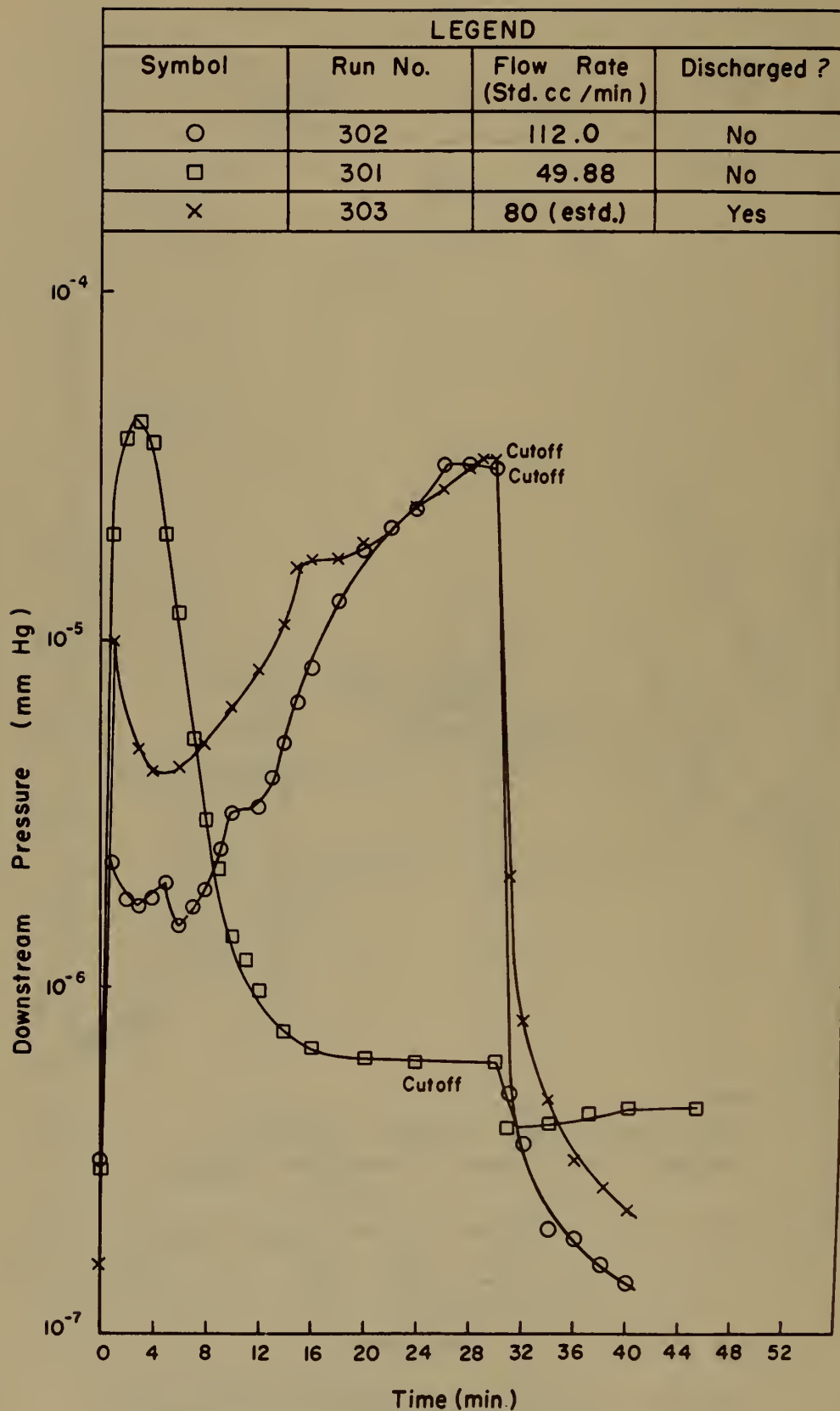


Figure 8. Variation of downstream pressure during deposition of ground-state and excited oxygen.

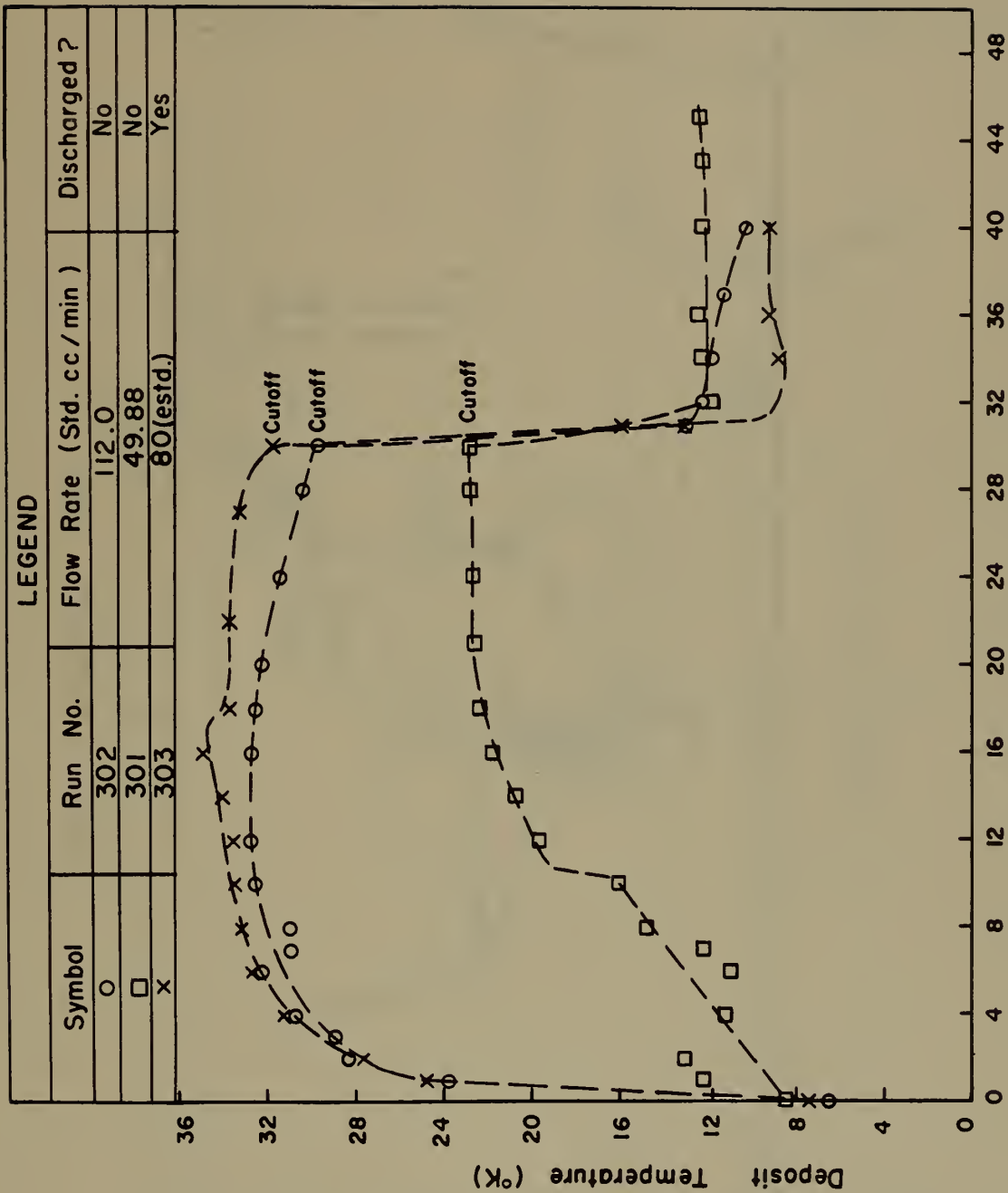


Figure 9. Variation of deposit temperature during deposition of ground-state and excited oxygen.

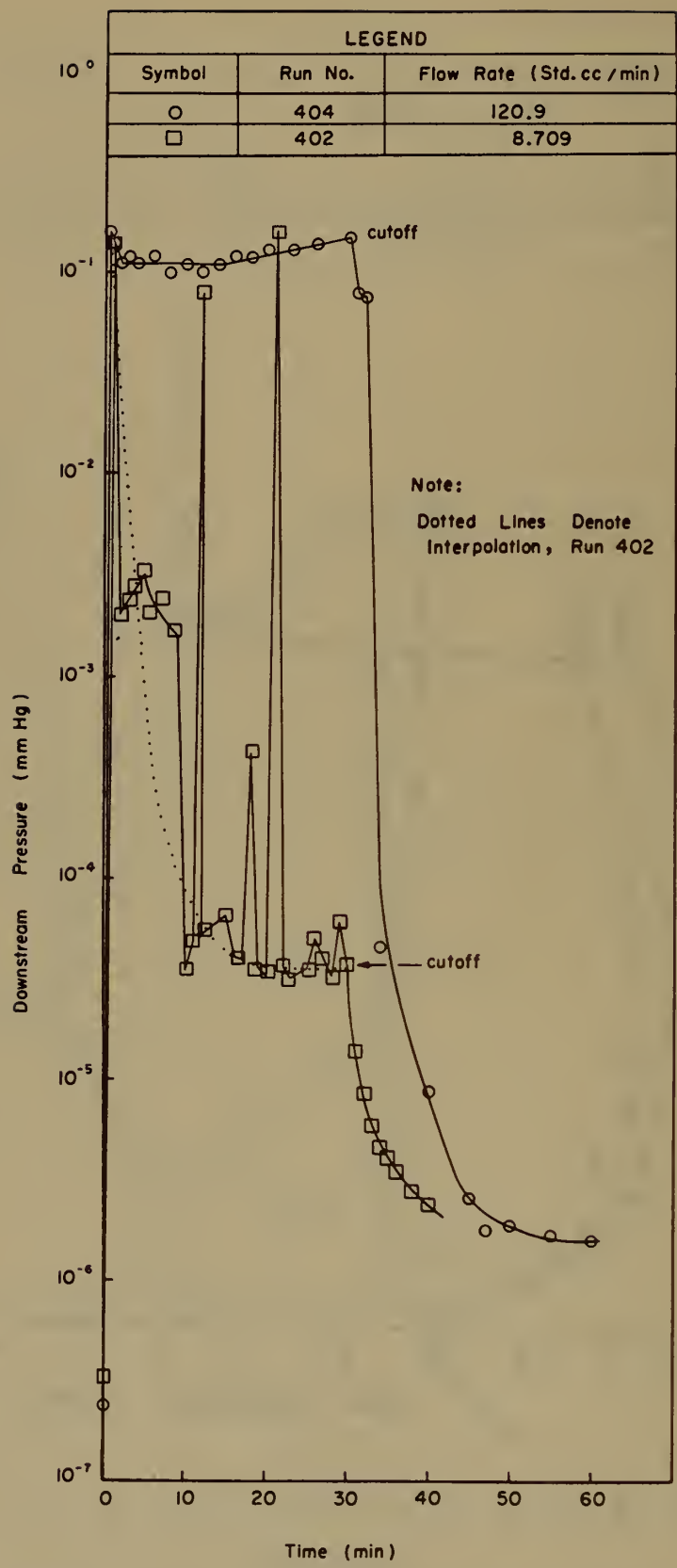


Figure 10. Variation of downstream pressure during deposition of ground-state hydrogen.

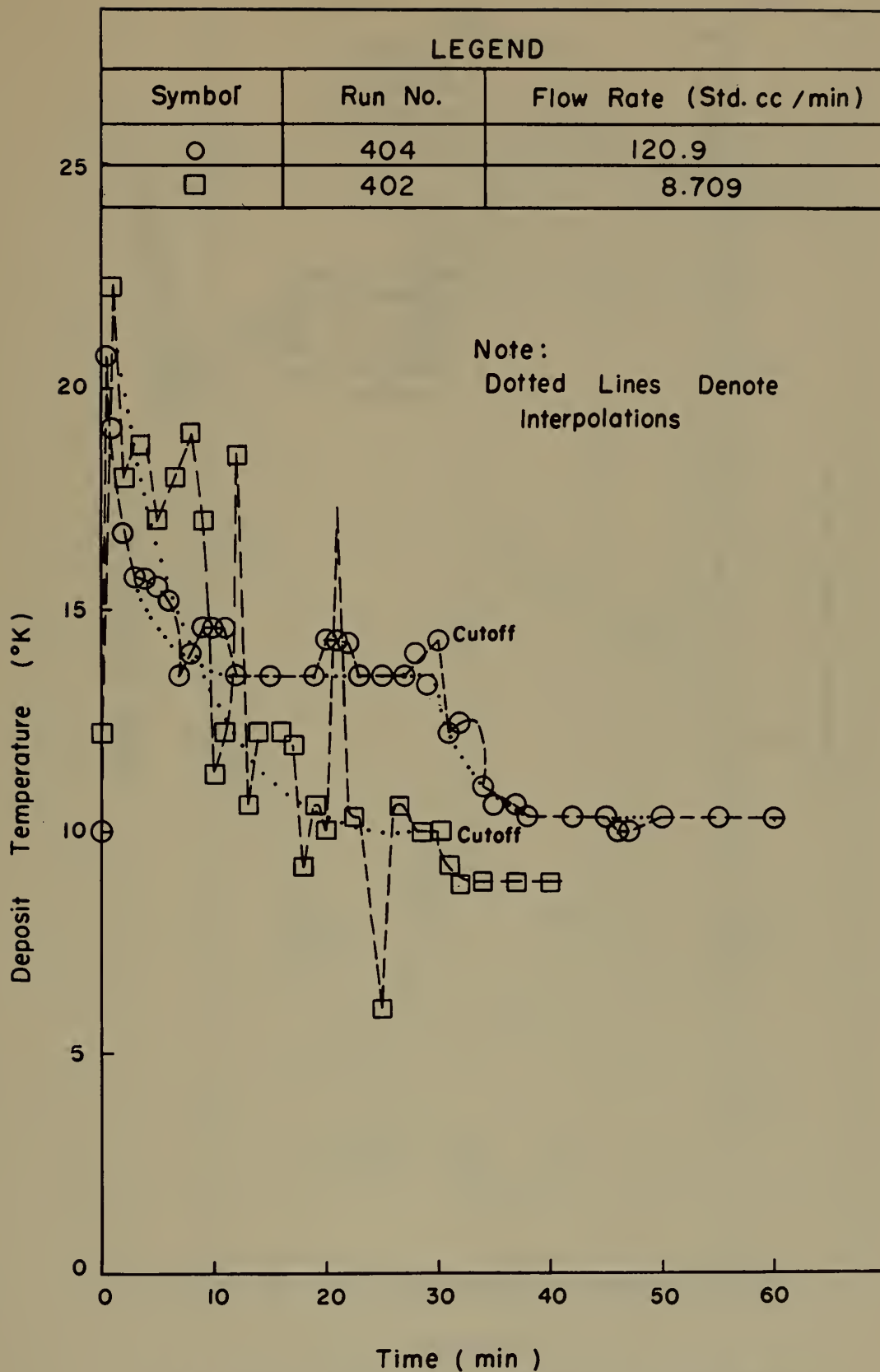


Figure 11. Variation of deposit temperature during deposition of ground-state hydrogen.

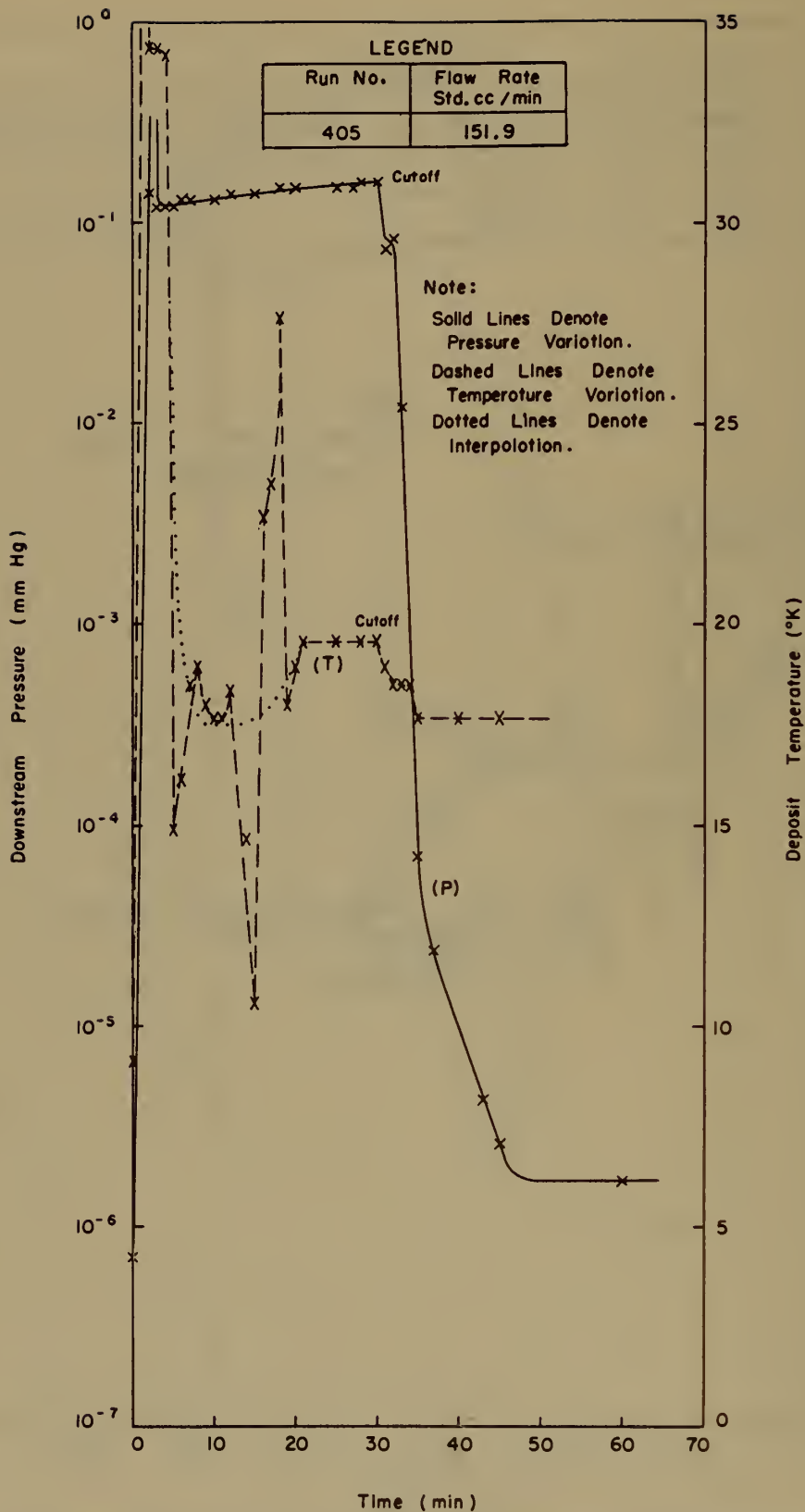


Figure 12. Variation of downstream pressure and deposit temperature during deposition of excited hydrogen.

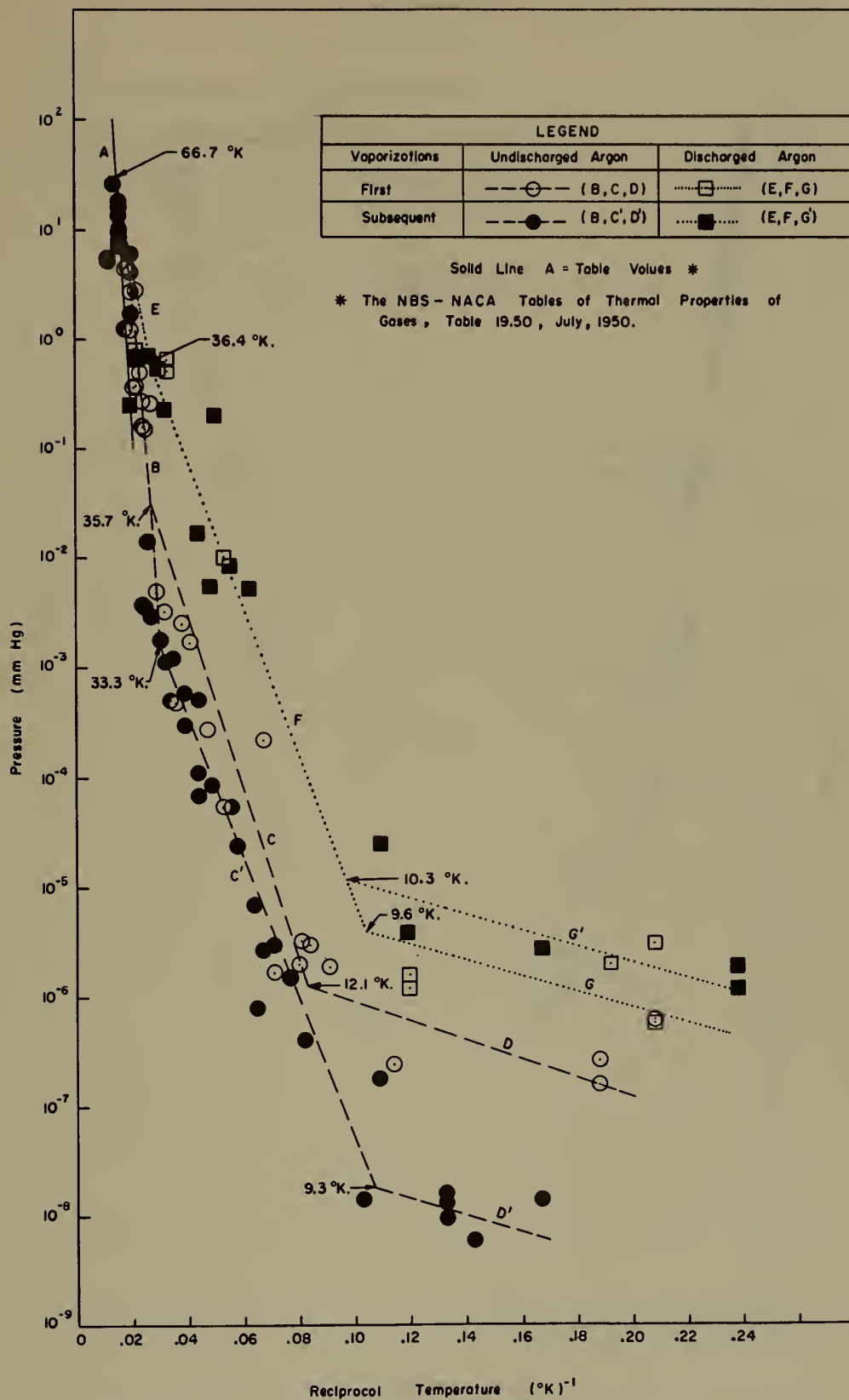


Figure 13. Warm-up curves for all argon deposits.

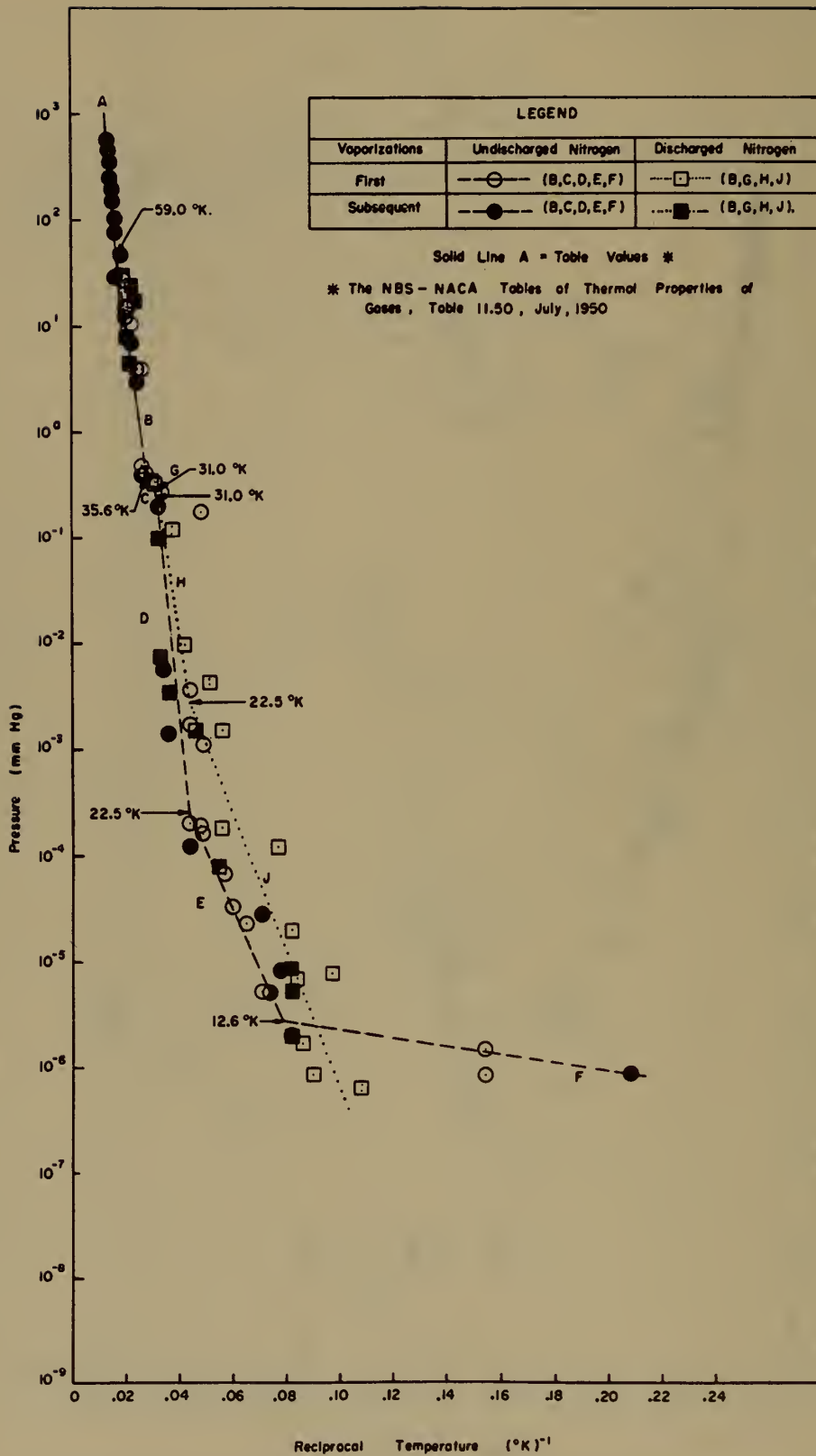


Figure 14. Warm-up curves for all nitrogen deposits.

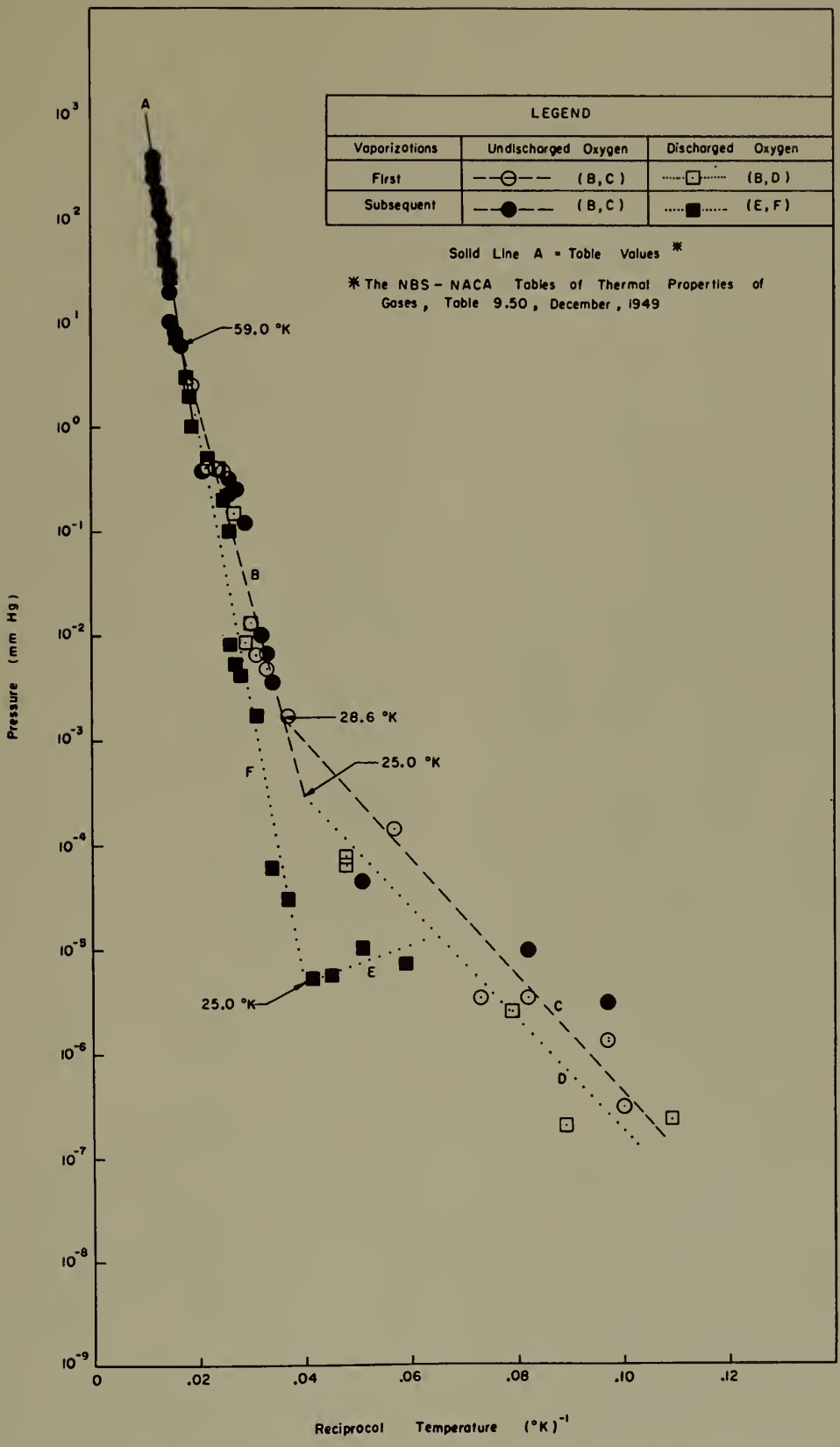
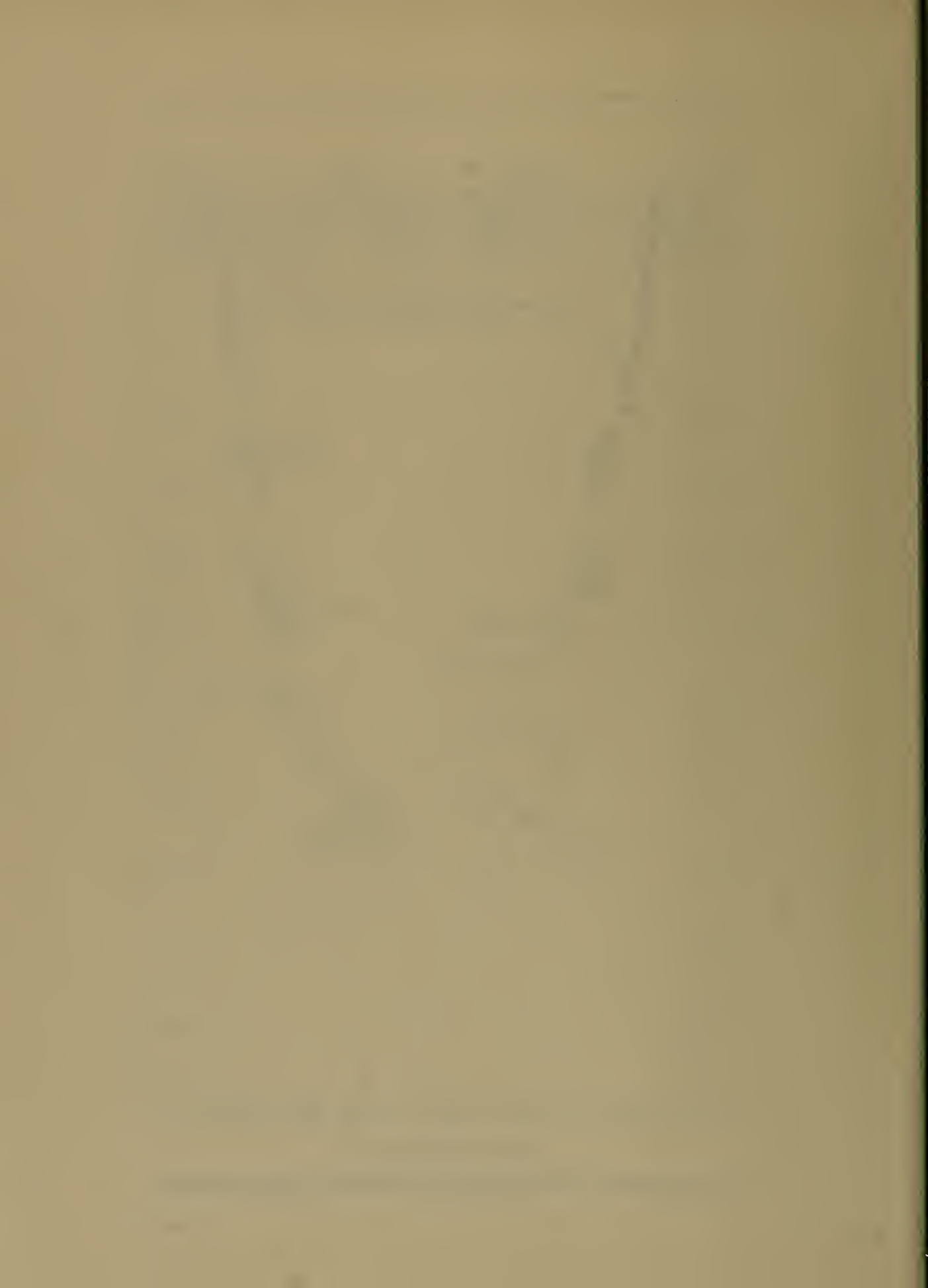


Figure 15. Warm-up curves for all oxygen deposits.



U.S. DEPARTMENT OF COMMERCE

Frederick H. Mueller, *Secretary*

NATIONAL BUREAU OF STANDARDS

A. V. Astin, *Director*



THE NATIONAL BUREAU OF STANDARDS

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WASHINGTON, D.C.

ELECTRICITY. Resistance and Reactance. Electrochemistry. Electrical Instruments. Magnetic Measurements. Dielectrics.

METROLOGY. Photometry and Colorimetry. Refractometry. Photographic Research. Length. Engineering Metrology. Mass and Scale. Volumetry and Densimetry.

HEAT. Temperature Physics. Heat Measurements. Cryogenic Physics. Rheology. Molecular Kinetics. Free Radicals Research. Equation of State. Statistical Physics. Molecular Spectroscopy.

RADIATION PHYSICS. X-Ray. Radioactivity. Radiation Theory. High Energy Radiation. Radiological Equipment. Nucleonic Instrumentation. Neutron Physics.

CHEMISTRY. Surface Chemistry. Organic Chemistry. Analytical Chemistry. Inorganic Chemistry. Electrodeposition. Molecular Structure and Properties of Gases. Physical Chemistry. Thermochemistry. Spectrochemistry. Pure Substances.

MECHANICS. Sound. Pressure and Vacuum. Fluid Mechanics. Engineering Mechanics. Combustion Controls. **ORGANIC AND FIBROUS MATERIALS.** Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Plastics. Dental Research.

METALLURGY. Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion. Metal Physics.

MINERAL PRODUCTS. Engineering Ceramics. Glass. Refractories. Enameled Metals. Constitution and Microstructure.

BUILDING RESEARCH. Structural Engineering. Fire Research. Mechanical Systems. Organic Building Materials. Codes and Safety Standards. Heat Transfer. Inorganic Building Materials.

APPLIED MATHEMATICS. Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics.

DATA PROCESSING SYSTEMS. Components and Techniques. Digital Circuitry. Digital Systems. Analog Systems. Applications Engineering.

ATOMIC PHYSICS. Spectroscopy. Radiometry. Mass Spectrometry. Solid State Physics. Electron Physics. Atomic Physics.

INSTRUMENTATION. Engineering Electronics. Electron Devices. Electronic Instrumentation. Mechanical Instruments. Basic Instrumentation.

Office of Weights and Measures.

BOULDER, COLO.

CRYOGENIC ENGINEERING. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Gas Liquefaction.

IONOSPHERE RESEARCH AND PROPAGATION. Low Frequency and Very Low Frequency Research. Ionosphere Research. Prediction Services. Sun-Earth Relationships. Field Engineering. Radio Warning Services.

RADIO PROPAGATION ENGINEERING. Data Reduction Instrumentation. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Propagation-Terrain Effects. Radio-Meteorology. Lower Atmosphere Physics.

RADIO STANDARDS. High frequency Electrical Standards. Radio Broadcast Service. Radio and Microwave Materials. Atomic Frequency and Time Standards. Electronic Calibration Center. Millimeter-Wave Research. Microwave Circuit Standards.

RADIO SYSTEMS. High Frequency and Very High Frequency Research. Modulation Research. Antenna Research. Navigation Systems. Space Telecommunications.

UPPER ATMOSPHERE AND SPACE PHYSICS. Upper Atmosphere and Plasma Physics. Ionosphere and Exosphere Scatter. Airglow and Aurora. Ionospheric Radio Astronomy.

