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MOLECULAR-BEAM DEPOSITION OF
NICKEL CHLORIDE ON METAL SUBSTRATES

by

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ABSTRACT

Sticking coefficients of nickel chloride on polycrystalline molybdenum, gold, and nickel have been measured by exposing the metal targets, over a range of 80-750°K, to a molecular beam of NiCl_2 at 836°K. Each target, heated to a constant temperature by a radiometer-controlled electron gun, was enclosed in a liquid-nitrogen-cooled collector for the capture of molecules reevaporated from the heated surface. The total amount of NiCl_2 striking the target in each 90-min exposure corresponded to $\gg 30$ monomolecular layers on the substrate. The coefficient-versus-temperature curve differed drastically from the corresponding theoretical curve calculated on the basis of equilibrium vapor pressure and beam geometry. Whereas the theoretical coefficient changed from near unity to zero over a span of about 60°, the experimental coefficient did so over 265°. Within the range of variation, the coefficient was significantly enhanced by a thin coating of NiCl_2 (>30 monomolecular layers) predeposited at 80°K. No systematic variation of the coefficient with duration of exposure was detected. The microscopic appearance of the deposit (at 100X magnification) was influenced by grain orientation of the polycrystalline metal-substrate. When gold targets were used, an incomplete recovery of total nickel indicated diffusion into the substrate.

I. INTRODUCTION

Depending upon experimental conditions, gas-solid interactions may be characterized by complex combinations of kinetic processes. Some occurring simultaneously and some consecutively, such processes may include adsorption, condensation, dissociation, chemical reactions of gas-with-solid or gas-with-gas, surface diffusion, solid diffusion, reevaporation, thermal accommodation, etc. The interaction may involve a gas that is "noncondensable," such as hydrogen, CO, nitrogen, or xenon or a "condensable" vapor, such as gaseous sodium, zinc, gold, CdI_2 , or NiCl_2 . The solid may be any material of interest that is in the solid phase at the temperature of interest.

A great deal of complexity in the study of such systems can be removed by applying the molecular-beam technique, which isolates the system of interest from conditions of equilibrium with the gas phase. By this technique, the interaction is confined to an environment of high vacuum in which the gas (or vapor) molecules of known temperature and flux impinge upon the solid surface of known temperature.

This report describes work in which a molecular-beam approach was used in the study of the interaction between nickel chloride molecules and metal substrates of molybdenum, gold, and nickel. The processes given specific consideration in this study were condensation, reevaporation, thermal accommodation, and solid diffusion.

Chapter II deals primarily with the significance of the sticking coefficient in the study of vapor-solid interactions and provides a review of related publications, particularly those that have appeared within the last 10 years.

Inasmuch as the experimental apparatus was designed and assembled from several component systems, some of which were purchased and others of which were fabricated in shops of Argonne National Laboratory, Chapter III is devoted to its description. Chapter IV and the appendix are included to show how the apparatus was used to produce the experimental data presented (mostly graphically) in Chapter V.

Chapter VI is devoted to a discussion of the experimental results, and Chapter VII to conclusions that may be drawn from this study.

II. SIGNIFICANCE OF STICKING COEFFICIENT IN VAPOR-SOLID INTERACTIONS

A. Definition and Use of Sticking Coefficient

The experimental determination that is most often made in the study of vapor-solid interactions is the evaluation of the sticking coefficient, β , which is a measure of the probability of retention of the condensed vapor on the solid. As experimentally measured, the coefficient is an integrated property for a specified duration of exposure of the vapor to the solid. The duration may be a matter of hours or a fraction of a second. The theoretical sticking coefficient, to which experimental data can be compared, is expressed as the ratio

$$\beta = \frac{Z' - Z''}{Z'}, \quad (1)$$

where Z' is the arrival rate (in moles/sec) of the vapor molecules as they impinge upon the solid surface, and Z'' is the departure rate as they return to the gaseous phase.

The sticking coefficient is not ordinarily attributable to a single process in a vapor-solid interaction, but is rather the resultant of at least three phenomena: thermal accommodation of kinetic energy brought to the solid by the impinging vapor molecules, nucleation of adsorbed molecules to a condensed phase, and growth of a stabilized, condensed phase. Accordingly, the sticking coefficient is interrelated with coefficients of thermal accommodation, condensation, and evaporation.^{8,50}

Although the sticking coefficient may not correspond directly to a specific process in a vapor-solid interaction, it has been used by many investigators to establish limits in nonequilibrium behavior and to test the validity of theoretical treatments of thermal accommodation, nucleation, and growth of condensed phases in heterogeneous systems.

As an example of establishing limits in nonequilibrium behavior, in a heterogeneous system of a vapor of one component condensing on the solid surface of another component, the sticking coefficient can reveal the extent of departure from equilibrium behavior of condensation of the vapor onto a crystal face of its own solid phase. In a one-component, two-phase system at equilibrium, the arrival and departure rates of molecules across a vapor-solid interface are equal. It is therefore expected that when a vapor of constant flux is impinged on a target of its own solid phase, the temperature of which is lowered to correspond to an equilibrium departure rate that is slightly less than the arrival rate, net condensation should occur and the sticking coefficient should increase from $\beta = 0$ to $\beta > 0$.

Actually, in molecular-beam experimentation with heterogeneous systems, condensation may occur only when the arrival rate is many orders of magnitude greater than the equilibrium evaporation rate. (See discussion in Ref. 41.)

This situation has given rise to the use of a parameter called the supersaturation ratio

$$s = \frac{Z'}{Z_e}, \quad (2)$$

in which Z_e is the equilibrium evaporation rate at the phase interface of an equilibrated, homogeneous, vapor-solid system of the vapor component at the substrate temperature. The supersaturation ratio, above which stabilized condensation occurs ($\beta > 0$), and below which no stabilized condensation occurs ($\beta = 0$), is called the critical supersaturation ratio.

Besides revealing the magnitude of the critical supersaturation ratio for a given system, the experimentally determined sticking coefficient may also yield useful information on parameters that affect the rate of condensation when the critical supersaturation is exceeded. Such parameters are target temperature, beam temperature, beam flux, crystalline nature of the surface, thickness of the condensate, and background pressure in the vacuum chamber.

B. Parameters of Sticking Coefficient

1. Target Temperature

Evseev and Ozhegov⁷ found that the sticking coefficient of antimony on glass varied inversely with target temperature over the range of 448-505°K. Inuzuka and Ueda²¹ observed a decline in β from about 0.75 to about 0.25 for gold on NaCl (cleaved in vacuum) over the target-temperature range 473-673°K, and a constancy at ~ 0.75 from 223 to 473°K. Henning,¹⁷ also working with gold on single crystals of NaCl, found the coefficient to approach unity at about room temperature and to become very small above 673°K.

2. Beam Temperature

In 1960, Sears and Cahn⁴¹ predicted, on the basis of their postulate that the temperature of the adsorbed beam molecules lies at some level between the temperatures of the substrate and the beam, that, for constant beam intensity and fixed substrate temperature, there is a critical beam temperature above which nucleation will not occur ($\beta = 0$) and below which nucleation will occur ($\beta > 0$). In 1964, Hruska and Pound¹⁹ and Shade⁴² reported that, by the use of double-oven effusion cells, which allowed

independent variation of beam temperature at constant beam flux, beam-temperature variation had no effect on critical supersaturation. Hruska and Pound were working with a beam of cadmium impinging on targets of copper and glass; Shade experimented with cadmium on targets of 0.025-mm polystyrene film, bonded to metal plates. However, in 1966, Ruth, Moazed, and Hirth,³⁸ also using a double-oven cell for beam deposition of zinc onto substrates of mica, lithium fluoride, and Pyrex glass, demonstrated that the beam temperature did affect the critical supersaturation for nucleation on all three substrates. They demonstrated that at a constant target temperature and a constant beam flux a rise in beam temperature could change $\beta > 0$ to $\beta = 0$. To confuse the issue somewhat further, Evseev and Ozhegov⁷ reported in 1967 that with tetratomic-antimony beam molecules, the critical condensation temperature (i.e., the maximum substrate temperature at which condensation occurs on a glass substrate at a fixed density of the molecular beam) increases with increase of beam temperature. In other words, if the substrate temperature should be held constant, an increase in beam temperature would change $\beta = 0$ to $\beta > 0$. The authors suggested that this apparent anomaly was in some way related to the dissociation of Sb_4 on the surface.

3. Beam Flux

Walton, Rhodin, and Rollins⁴⁶ studied the nucleation rate of vaporized silver onto a sodium chloride substrate as a function of incidence rate; Inuzuka and Ueda²¹ later made a similar study. The rate of nucleation (with a corresponding effect on β) was shown to increase very rapidly with beam density under conditions equivalent to constant temperatures of beam and substrate.

4. Surface Properties

Physical properties of the solid surface apparently can have a significant influence upon the measured sticking coefficient of an impinging vapor. For example, Yang, Simnad, and Pound⁵³ found that the coefficients for the condensation of silver on silver, gold, platinum, nickel, and glass were 1.00, 0.99, 0.86, 0.64, and 0.31, respectively. They attributed the nonunity values to lattice misfit between condensate and substrate. Chakraverty and Pound⁴ proposed a theoretical model, based on the contact angle between a growing nucleus and the substrate, to explain the apparent effects of macroscopic steps in the surface on condensation. Inuzuka and Ueda²¹ concluded that nucleation of gold on vacuum-cleaved NaCl surfaces occurred preferentially at imperfection sites, such as point defects and impurities, and that it occurred at random sites on defect-free surfaces at relatively higher deposition rates.

5. Thickness of Condensate

Bachmann and Shin² determined that dependence of the sticking coefficient on the thickness of deposits of silver and gold, evaporated onto a layer of SiO on a quartz crystal, was such that $\beta = 1$ when the mean thickness of the deposit exceeded 10 Å for silver and 20 Å for gold, and that β averaged only 0.81 for silver in the thickness range of 0-10 Å, and 0.89 for gold in the thickness range 0-20 Å. Working with deposits of less than one monolayer of silver on gold and on glass substrates, Yang, Simnad, and Pound⁵³ observed that although the coefficient was unity for all measurements on gold, it increased with duration of exposure on glass, especially at the higher beam fluxes of their experimental variations.

6. Background Pressure

Schwarz⁴⁰ obtained data, in experiments with silver deposition on SiO films, that indicated strong dependence of the sticking probability on background pressure, especially during early stages of film formation. He concluded that the initial sticking coefficient can be smaller by a factor of about 30 at 10^{-5} Torr as compared to 5×10^{-10} Torr.

C. Measurement of Sticking Coefficient

Methods used in recent experimental investigations (with no claim to an infallible inclusion of all pertinent ones) include quartz-crystal-oscillator-rate monitoring technique,^{2,40} radioactive-tracer technique,⁵³ gravimetric technique,⁷ visual detection,^{38,42} electron microscopy,^{3,36,46,54} and colorimetric analysis.¹⁹

Earlier work involving the determination of sticking probabilities and/or critical supersaturations, in the study of vapor-solid interactions, is extensively reviewed by Hirth and Pound,¹⁸ Wexler,⁴⁹ and Estermann.⁶

D. Thermal Accommodation

As pointed out earlier, one of the phenomena involved in a vapor-solid interaction that can affect experimentally determined sticking coefficients is thermal accommodation. Originally introduced by Knudsen²³ to describe the degree of thermal equilibrium between the substrate surface and the molecules incident onto and subsequently ejected from it, thermal accommodation is usually expressed by the coefficient

$$\alpha_T = \frac{T_I - T_R}{T_I - T_S}, \quad (3)$$

where T_I , T_R , and T_S are the temperatures of the incident molecules, of the molecules restituted to the gas phase (either by reflection or by reevaporation), and of the substrate respectively. Reviews of earlier

theoretical work (e.g., Chapter A of Ref. 18) show that restitution of impinging molecules by reflection is of insignificance in vapor-substrate systems where the vapor is that of a metal or other crystalline solid. This leaves reevaporation as the only significant mechanism that can lead to incomplete thermal accommodation. Further, even in reevaporation, thermal accommodation is incomplete only if $T_R \neq T_S$.

Inasmuch as the effect of any reevaporation, whether at $T_R = T_S$ or $T_R \neq T_S$, shows up in the experimentally determined sticking coefficient, it becomes obvious that reevaporation must be incorporated in nucleation theory. However, not until Sears and Cahn⁴¹ suggested that the mean temperature of adsorbed molecules, involved in the nucleation process, was higher than the substrate temperature, had there been much concern over the relationship of thermal accommodation to nucleation. Certainly, if the idea of Sears and Cahn were valid, then nucleation calculations should be based upon T_A (temperature of adsorbed molecules) rather than upon T_S , and T_A should be a function of T_I .

The proposed model that allowed $T_A > T_S$ was based on two characteristic times: τ_R , the relaxation time required for accommodation of the kinetic energy of the impinged molecule into the vibrational modes of the surface; and τ_S , the mean time of stay for molecules on the surface before thermal desorption. If τ_R is long compared to τ_S , desorption occurs before the vapor material comes to thermal equilibrium with the surface, thus allowing the reevaporated molecules to have an average kinetic temperature between that of the incoming vapor and that of the surface.

Since Sears and Cahn's proposal was published in 1960, at least two publications^{19,42} offered unfavorable experimental evidence, and at least two later ones^{38,39} offered favorable evidence.

Advances in theoretical treatments of thermal accommodations have steadily continued in recent years. Approaches to a better understanding of the phenomenon from the standpoint of atomistic mechanisms have been based on various models, namely, linear-chain lattice,^{29,30} two-dimensional lattice,⁵ three-dimensional lattice,^{11,12} and independent surface-atom oscillator.^{26,27} Studies have been made on the theoretical separation and correlation of the translational and internal components of the kinetic energy of the vapor molecules that is converted into vibrational excitation of the substrate lattice.^{1,9} Also, the effect of surface-adsorbed molecules on the thermal accommodation of impinging molecules has been theoretically explored.^{28,43}

E. Nucleation

Over a period of nearly half a century, a nucleation theory has evolved that is based upon a phenomenological approach by which thermodynamic

properties of the bulk form of the condensate are applied to newly formed particles on the substrate. Only within the last decade has a second approach to nucleation theory, based on statistical mechanics, come to share consideration with the older "classical" one.

1. Phenomenological Theory

Hirth and Pound^{18,37} presented the phenomenological or classical theory and its historical background in detail. Based on a thermodynamical development, the theory essentially consists of four steps: (a) Determine the density of molecular clusters of the condensed phase that would be in equilibrium with the supersaturated vapor if nucleation did not take place; (b) find the size of the cluster that has an equal probability of growing larger or smaller, i.e., the critical nucleus; (c) after correcting the information obtained in step a for the departure from equilibrium due to nucleation, determine the concentration of critical nuclei; and (d) multiply this concentration by the arrival rate of the incident molecules to obtain the rate of nucleation.

Two assumptions originally used in the theory have been open to question. One was that the critical nucleus was cap-shaped; the other, that its surface energy was identical to that of the bulk material. Subsequent calculations of nucleation rate based on the assumption of a disk-shaped nucleus¹⁸ reportedly have afforded better agreement with experimental data.³⁸ Although the objectionable feature of ascribing bulk surface-energy properties to clusters of only a few molecules remained, the theory has been related successfully to experimental data.^{18-20,38}

2. Statistical Theory

In 1962, Walton⁴⁵ reported a statistical-mechanical approach to nucleation theory by which he obtained an expression for nucleation rate that was valid for very small clusters, even as small as one molecule. He calculated the concentration of clusters at equilibrium by means of a partition function for a two-dimensional adsorbed gas composed of different molecules, each molecule corresponding to a cluster of a given size and structure. According to Walton's procedure, the most probable distribution of clusters of different sizes is obtained from the partition function. The clusters that are critical nuclei correspond to the minimum of the distribution function. The population of such critical nuclei is then multiplied by the rate of impingement to give the nucleation rate.

Walton also pointed out that the small size of the nucleus has an important effect on the orientation of the resulting deposit of condensate.

Walton, Rhodin, and Rollins⁴⁶ experimentally tested the new expression for nucleation rate by studying the deposition of silver vapor onto a freshly cleaved surface of sodium chloride as a function of substrate temperature and of incidence rate. The expression was valid where the nucleus was expected to be very small (e.g., in one case, the nucleus was composed of one atom, and in another, three atoms). Expressions taken from this theoretical development were also used to deduce the binding energy of a silver atom to a sodium cleavage face, the dissociation energy of the three-atom critical nucleus, and the activation energy for diffusion of a silver atom on a [100] sodium chloride surface.

Inuzuka and Ueda²¹ applied the theory in the study of gold deposits on substrates of cleaved crystals of NaCl and of KCl. Halpern¹⁵ extended calculations of the statistical concept and concluded that the growth of the deposit of condensed vapor on a substrate is affected by the nature of the small clusters of atoms formed initially.

As might be expected, the proponents of the two approaches to nucleation theory have not always been in agreement regarding the most satisfactory interpretation of experimental data.^{14,32} Kenty²² used classical nucleation theory to analyze the data of Walton *et al.*⁴⁶ and concluded that, since a "Pound plot" of the data produces a straight line, the data are interpretable by the formalism of the classical theory.

Poppa³⁶ and Moore³³ have reviewed the two theories with pertinent references to previous investigations that have contributed to the present state of affairs. Poppa tested the two theories using in situ electron-microscopic studies of the heterogeneous nucleation of bismuth and silver on amorphous substrates as a function of substrate temperature and impinging flux. Both theoretical concepts led to specific conclusions concerning such nucleation parameters as the number of atoms in the critical nucleus, n^* , and the free energy of desorption, ΔG_{des} . The statistical-mechanical treatment indicated that in the range of 475-625°K, n^* was from one to three and ΔG_{des} was from 6 to 40 kcal/mole. By using appropriate approximations, the classical treatment yielded comparable numbers for n^* , and values higher by a factor of about 1.7 for ΔG_{des} .

Gretz¹³ reported still another mechanism of nucleation, which involves a random creation of nuclei that are promoted to critical nuclei by direct impingement of molecules from the vapor. The predicted nucleation rate is reportedly in agreement with Walton's data for nucleation of silver on NaCl.

F. Growth of Condensate Particles

With the population of growing nuclei established on the substrate surface as a function of substrate temperature, beam temperature, and beam flux,

growth occurs in proportion to the product of the growing-nuclei population and the beam flux. Bassett³ observed, in an electron-microscopic study of nucleation and growth of silver and copper on carbon film, that the vast majority of nuclei appeared to be formed simultaneously, and that after deposition had been proceeding for about 1 min, a newly-formed nucleus was rarely observed. In a similar electron-microscopic study of bismuth on an evaporated carbon substrate, Poppa³⁶ observed a rapid increase in the population of bismuth particles during the first few seconds of exposure of the beam to the substrate, and then a leveling off to constancy with duration of exposure. The experiment was made at four different substrate temperatures, and the level of constancy in population was found to vary inversely with the temperature of the substrate.

Hirth and Pound¹⁸ give a comprehensive discussion of the growth of nucleated condensates.

G. Features of Investigation

A primary goal of this investigation was to study the sticking coefficient of the vapor of a nonmetallic compound impinging onto a metallic substrate as a function of substrate temperature and of duration of exposure.

Table I lists some literature references encountered in a review of experimental work performed within the last 10 years relating to the determination of sticking coefficients of condensible vapors (gases not included) on various substrates. None of these systems deals with the condensation of nonmetallic material on metallic substrates. A search of earlier

TABLE I. A Review of Vapor-Substrate Systems since 1959

Vapors	Substrates	Reference
Bi, Pb, Sn	Glass	35
Cd	Polystyrene film	42
Au	NaCl	17, 21
Ag	NaCl	46
Sb ₄	Glass	7
CdI ₂	Amorphous carbon	54
Ag, Cu	Carbon film	3
Ag	MoS ₂	3
Bi, Ag	Amorphous substrates	36
Zn	Mica, LiF, glass	38
Zn, Cd	Glass	20
Ag, Au	SiO film	2, 40
Cd	Copper, glass	19
Cd	Tungsten	39

literature revealed that very little information has been reported on systems of nonmetallic vapors on metallic substrates since 1939, when Hayward¹⁶ studied the condensation of salicylic acid, mercuric iodide, anthracene, iodine, and stannic iodide on a copper surface.

It is generally accepted that the thermal-accommodation coefficient is approximately unity for a metal vapor impinging onto a clean metal substrate. Furthermore, on nonmetallic substrates, there is good evidence of incomplete thermal accommodation, for either metallic or nonmetallic vapors (as discussed in Section D above). Little information is available, however, on how important the role of accommodation coefficient may be in the condensation of nonmetallic vapors on metallic substrates.

In this study, the rapid heat drain provided by the high thermal conductivity and heat capacity of the massive metal target tends to shorten the relaxation time, τ_r , allowing the thermal-accommodation coefficient to approach unity, and leaving the sticking coefficient to be a more specific description of the nucleation process.

A second goal of this investigation was to look for evidence of the nucleation process by "seeding" the clean metal substrate with a pre-deposit of densely populated nucleation sites of NiCl_2 .

An apparatus was developed to measure the total amount of NiCl_2 vapor, incident to the substrate target, thus avoiding some of the surmised uncertainties involved in the calculation of incident-vapor flux, based on beam geometry and on the distribution laws of effusion phenomena.^{47,48,51,52}

III. APPARATUS

The apparatus was designed for sequential exposures of a series of metal targets, each at a specified, controlled temperature, and each surrounded by a liquid-nitrogen-cooled collection chamber for retention of reevaporating molecules. The equipment included an effusion cell; beam-defining components, to produce a molecular beam of NiCl_2 of known geometry and flux; a controlled induction-heating system, to maintain the effusion cell at a known temperature; a controlled electron-gun heating system, to hold each target at temperature T (300-800°K) for 90-min exposures; a thermocouple system; a system for circulating liquid nitrogen; and a vacuum system, for experimentation at about 10^{-8} Torr.

Figure 1 is a sketch of the vacuum chamber. The cutaway view reveals the orientation of the beam components and of one of the electron guns used for heating the targets. The photograph in Fig. 2 gives an overall view of the physical arrangement of the apparatus in the laboratory; and Fig. 3, a closeup view of the electron-gun area.

A more detailed description of each system of the apparatus follows.

A. Molecular-beam System

Figure 4 is a diagram of the arrangement of the component parts of the molecular-beam system. Nickel chloride vaporizes in the inductively heated, platinum effusion cell, and the gaseous NiCl_2 molecules that strike the temperature-controlled metal target pass successively through the orifices of the cell, the chill block, the shutter, and the chilled wall on which the target magazine is mounted. The first and last of these orifices determine the geometry of the beam.

1. Description of Beam Components

The effusion cell is supported within the induction-heating coil by a section of fused-silica tubing that is secured to structural framing by spring-loaded clamps, which afford x, y, and z motional adjustment. The cylindrical cell wall is 22.2 mm long, 7.92 mm ID, and 11.1 mm OD. The flanged base (which is keyed into the glass tubing to secure its position) and the flanged lid, each 3.18 mm thick, are fastened together by three equally spaced stainless steel bolts. Two thermocouples are located in wells drilled into the central area of the base flange. Each thermocouple is secured by a setscrew that enters the cylindrical side of the flange, perpendicular to the well. A grounding wire is attached to the cell by a stainless steel screw, which is also mounted on the base flange.

The gold-plated copper chill block, cooled by circulating liquid nitrogen, captures most of the effusate that is not included in the defined

beam path, thereby preventing unnecessary contamination of the vacuum chamber. A fused-quartz glass-tubing sleeve, enclosing the cell within the heating coil, serves as a shield to wide-angle rays of effusate and increases the completeness of containment.

121-4971

Fig. 1. Vacuum Chamber. Cutaway shows molecular-beam apparatus and one electron gun.

121-4460

Fig. 2. Overall View of Molecular-beam Apparatus

121-4459

Fig. 3. Electron-gun Area

121-4460

Fig. 2. Overall View of Molecular-beam Apparatus

121-4459

Fig. 3. Electron-gun Area

beam, is precisely indicated by an indexed dial, attached to the worm-gear mechanism outside the chamber.

121-4560

Fig. 6. Target and Collector Cavity

Each target is centered within and near the outer end of a cylindrical cavity in the magazine, as shown in Fig. 6. This cavity, called the collector in this report, is maintained at liquid-nitrogen temperature during experimentation. Geometrically, the cavity intercepts 95% of the material that leaves the target surface, according to a cosine distribution of reevaporating molecules. Three pins, visible in Fig. 6, hold each target in position. One is a 1-cm length of fused-silica rod, pointed on one end to fit into the peripheral groove of the target. The other two are tungsten wires, which are glass-coated only in the area in which they are held in place by setscrews. The uncoated "tails" make sufficient contact with the magazine chassis to provide the necessary electrical grounding for each target. The glass insulation on the pins, in close proximity to the heated target, prevents excessive heat drain by conduction from the target into the chilled support.

2. Beam Geometry

The size and the shape of the molecular beam are determined by the circular cross-sectional areas of the cell orifice, the circular

cross-sectional area of the defining aperture, and the distance between them. Accordingly, the size of the deposit on the target depends upon the distance from the defining aperture. The fraction of restituted beam molecules intercepted by the collector depends upon the diameter of the collector and the distance from the target to the opposite open end of the collector. Table II lists the geometrical dimensions that prevailed during the experimentation described in this report. The diameters of the orifice and the defining aperture were measured with a movable-stage microscope micrometer.

TABLE II. Dimensions of Beam System

Distance from cell orifice to defining orifice, $d_1 = 4.45$ cm
Distance from defining orifice to target, $d_2 = 4.45$ cm
Radius of cell orifice, $r_1 = 0.02239$ cm
Radius of defining aperture, $r_2 = 0.2124$ cm
Radius of deposit on target, $r_3 = \frac{d_1 + d_2}{d_1} r_2 = 0.425$ cm
Area of cell orifice, $a_1 = \pi r_1^2 = 1.575 \times 10^{-3}$ cm ²
Area of defining aperture, $a_2 = \pi r_2^2 = 0.1417$ cm ²
Area of deposit on target, $a_3 = \pi r_3^2 = 0.567$ cm ²

3. Calculations of Kinetic Rates

The rate of effusion from the cell and the rate of arrival at the target can be calculated from a knowledge of the beam geometry, the molecular weight, the temperature, and the pressure of the NiCl_2 vapor in the cell. Furthermore, the rate of departure from the target can be estimated

from the cross-section area and the temperature of the deposit on the target. Then the difference between the arrival rate and departure rate constitutes a calculated estimate of the deposition rate of the beam molecules on the target at a specified temperature. An objective of this investigation was to compare such theoretically calculated rates of deposition with experimentally determined rates, obtained by measurement of the quantity of beam-deposited material collected on each target in a measured interval of time.

The rate of effusion of molecules from the cell orifice in moles per second is given by

$$Z = \frac{pa_1c}{(2\pi MRT)^{1/2}}, \quad (4)$$

where p is the pressure of the NiCl_2 vapor in the cell, in dynes/cm²; a_1 is the area of the cell orifice, in cm²; M is the molecular weight; T is the cell temperature, in degrees Kelvin; R is the gas constant (8.3144×10^7 ergs per degree per mole); and c is the probability of transmission of the molecules through a nonideal orifice (nonideal in the sense that the pipe composing the orifice is of finite length). With the constants collected and with the pressure expressed in Torr, Eq. 4 becomes

$$Z = 0.0583pa_1c(MT)^{-1/2} \text{ mol/sec.} \quad (5)$$

From the electronically controlled constant temperature of the cell, the equilibrium pressure p is derived, using the thermodynamic data of McCreary and Thorn³¹ for NiCl_2 (550-608°C), represented by the equation

$$RT \ln p = -(53.59 \pm 0.41) \cdot 10^3 + (43.70 \pm 0.48) T, \quad (6)$$

where R is in cal/mole-degree and p in atmospheres.

Table III lists the calculated effusion rate, Z , with some of the parameters and constants on which it is based for the experimentation reported here. The vapor pressure of NiCl_2 in the effusion cell is calculated from Eq. 6. The Clausing factor, c , is assumed to be unity because, even for nonideal orifices, the effective deviation from the cosine distribution in the forward direction, along the axis normal to the orifice, is negligible.¹⁰

The arrival rate, Z' , of the molecules at the target is a small fraction of the total effusion rate;¹⁰ namely,

$$Z' = \frac{a_2}{a_2 + \pi d_1^2} Z \text{ moles/sec} \quad (7)$$

where a_2 is the area of the defining orifice, and d_1 is the distance from the orifice to the defining aperture.

TABLE III. Effusion Rate and Parameters

Temperature of effusion cell	$T = 836^\circ\text{K}$
Vapor pressure of NiCl_2 in cell	$p = 2.649 \times 10^{-2}$ Torr
Molecular weight of NiCl_2	$M = 129.6$ g/mole
Clausing factor	$c = 1.00$
Gas constant	$R = 8.314 \times 10^7$ ergs/mole-degree
Effusion rate	$Z = 7.39 \times 10^{-9}$ mole/sec
Arrival rate	$Z' = 1.68 \times 10^{-11}$ mole/sec

An approximate evaluation of the arrival rate in terms of monomolecular layers per second can be made by assuming closest-packed, standing-on-end orientation of the linear-shaped,^{24,34} gaseous, triatomic molecules. If the diameter of the elongated molecule is assumed to be about 2×10^{-8} cm, the resulting monomolecular layer density is approximately 4.8×10^{-9} moles/cm². The 0.567-cm² deposit area of the target then holds 2.7×10^{-9} moles of NiCl_2 in a monomolecular layer, and the arrival rate (given in Table III) amounts to about 6×10^{-3} monomolecular layers per second, or at least 30 monomolecular layers in 90 min.

The departure rate, Z'' , of beam molecules that strike the target and come to thermal equilibrium with it before reevaporation can be estimated as being identical to the rate of evaporation from an equivalent area of crystalline NiCl_2 at temperature T_2 ; namely,

$$Z'' = \frac{0.0583 p_2 a_3}{(M T_2)^{1/2}} = 2.90 \times 10^{-3} p_2 T_2^{-1/2}, \quad (8)$$

where p_2 is the equilibrium pressure of NiCl_2 at T_2 , and a_3 is the area of the deposit on the target.

The sticking coefficient, β , can then be evaluated throughout a temperature range as

$$\beta = \frac{Z' - Z''}{Z'}, \quad (9)$$

assuming the idealized system of the preceding paragraph in which the evaporation rate of NiCl_2 from a metal target is the same as that from a surface of crystalline NiCl_2 . A set of coefficients derived in this manner for the beam system described above was calculated for target temperatures of 0-800°K and is shown plotted against temperature in Fig. 7.

This estimation of theoretical sticking coefficients does not take into account molecules restituted to the gas phase with incomplete thermal accommodation. Nonetheless, it allows the use of the effusion equation, the thermodynamic vaporization equation for NiCl_2 , and the geometry of the beam apparatus to calculate a point of reference to which experimental data can be compared and related.

121-4968

Fig. 7. Theoretical Sticking Coefficient
vs Temperature of Target

beam-producing hardware is partially dismantled to allow access to all areas of condensate for light scraping and for minimal irrigation with water and methyl alcohol from plastic squirt bottles. Absorbent material is temporarily placed under the area of cleaning to protect other parts of the vacuum chamber from falling debris.

Also, when the vacuum chamber is opened for cleaning, the effusion cell is removed, cleaned, and recharged with a new supply of anhydrous NiCl_2 . The rate of depletion of NiCl_2 from the cell can be estimated from the calculated effusion rate (as discussed in Section 3 above), provided the source material is pure. If nickel oxide, or a hydrate of NiCl_2 (thermally decomposable to nickel oxide) is present in the cell, the residue, after several hours of operation, consists of amberish-brown crystals of NiCl_2 , covered over by an ashy shroud of nickel oxide.

After the cell and other beam components are replaced in their positions, the alignment of the cell, with respect to the defining aperture and the target, is checked by removing one of the targets and viewing the cell orifice along the axis of the beam path. Adequate alignment is indicated when all circular visible parts appear to be concentric to the eye, the cell orifice being at the center. If the visible parts are not concentric, setscrews in the cell-support mechanism are appropriately adjusted. The importance of locknuts on such setscrews became apparent during experimentation. Without them, vibrations allowed the setscrews to shift in position, resulting in misalignment and improperly exposed targets.

4. Operational Notes

Although the magazine is cleaned each time a set of targets is removed for analysis, the other components of the beam system are cleaned only after several exposures. At such a time, the bell jar is raised and the

B. Vacuum System

The high-vacuum system consists of a metal chamber formed by sealing a 12-in. Ultek ion pump (Model TNB, Ultek Division of Perkin-Elmer, Palo Alto, California) to a 22-in. stainless steel bell jar through an adapting flanged base, shown in Fig. 1. Attached to the high-vacuum chamber through a shutoff valve is a fore-vacuum line, consisting of a molecular-sieve trap, a Hivac-7 rotary pump (Cenco Instruments Corp., Chicago, Illinois), appropriate bellows-type vacuum valves, and a dry-nitrogen makeup line for relieving vacuum in the chamber.

1. High-vacuum Chamber

The high-vacuum chamber is designed to accommodate the molecular-beam components now in use as well as a velocity-selector apparatus which may be applied in future experimentation. The 22-in. flanged base affords support for structural framework on which the beam hardware is mounted, leaving the 12-in. throat of the ion pump essentially unobstructed.

The Ultek unit contains two pumps: one, a sublimator with a rated pumping speed of 3600 liters/sec, and the other, an ion pump with a rated speed of 50 liters/sec. It has ten service ports, eight of which accommodate the following equipment: the fore-vacuum line, a hot-cathode pressure-gauge tube, liquid-nitrogen supply and return lines, an rf feed-through for induction-heating lines, a multiple thermocouple feed-through, an electrical-power feed-through, and a rotary feed-through for operating the beam shutter.

The metal bell jar has a 6-in., flanged access port through which the target magazine is removed for analysis; two flanged ports for the two electron guns; one for the radiometer optics; one for visual inspection of the targets; and a small one at the rear of the chamber for viewing the effusion cell. Two 6-V, pilot-light lamp bulbs (stripped of all supporting material, down to glass and wire) are mounted inside the chamber for illumination during cell alignment and subsequent inspection.

Metal gaskets are used on all flanges, except on those of the 6-in. sample port and the 22-in. bell jar. Although these two flanges were designed to use metal gaskets, the excessive amount of time required to tighten the flange bolts with a torque wrench (6 hr or more for the bell-jar flange) to the point of negligible leakage (tested by a mass-spectrometer leak detector) led to the substitution of Viton O-ring gaskets. These O-rings are treated with Apiezon H grease (Associated Electrical Industries, Ltd., England) and are installed with metal spacers to protect the flange seats. The spacer for the 6-in. flange is in the form of a ring of smaller diameter

than the Viton O ring such that it also serves as a retainer for the O ring. Mounted on the inside diameter of this retainer ring are electrically insulated terminals at which the leads to the pilot test-target thermocouple are disconnected when the magazine is removed for analysis. The Viton O rings were supplied by Tech-Syn Corporation, Mt. Prospect, Illinois.

Independent measurements of the chamber pressure can be made by the Ultek-pump control unit (which indicates the pressure level as a function of the current flowing in the ion pump) and by a Baird-Alpert-type ion gauge with a Veeco (Type RG-3A) control unit (Veeco Instruments Inc., New York). The Ultek unit contains an overload relay, which shuts down the high-vacuum pump when the pressure exceeds about 10^{-6} Torr.

Heat is supplied to the vacuum chamber for bake-out through four voltage-controlled, heavy-insulated heater tapes, $3\frac{1}{4}$ in. wide by 72 in. long (supplied by A. Daigger and Co., Chicago, Illinois), and through a Calrod heater, clamped to the underside of the flanged base. During bake-out, the entire bell jar is wrapped with aluminum foil to provide insulation from convection and radiant-heat losses.

2. Fore-vacuum Line

Connected to the manifold of the fore-vacuum line that leads through a molecular-sieve trap to the mechanical pump is the shutoff valve to the high-vacuum chamber, a thermocouple-gauge tube, two valves to vacuum lines leading to the two rotary feed-through seals, and a dry-nitrogen supply line.

The fore-vacuum line remains in continuous operation to maintain vacuum on the shafts of the rotary feed-throughs. Each shaft, extending from atmospheric-pressure air outside the chamber to high vacuum inside the chamber, is fitted with two sealing O rings such that a small space between them is connected to the fore-vacuum system. The pressure in the manifold is monitored by the thermocouple gauge.

A dry-nitrogen supply protects the cathodes of the electron guns from damage by atmospheric moisture when the chamber is open. The details of the manipulation of the dry-nitrogen flow during shutdown and startup operations are given in the experimental procedures in Chapter IV.

C. Cell-temperature Control System

Figure 8 is a block diagram of the electronic feedback loop used to control the temperature of the effusion cell. The output of the control thermocouple attached to the cell is bucked against a reference dc signal. The net voltage (error signal) is amplified by a deviation amplifier and fed

into a current-adjusting type control unit that supplies current to a saturable reactor through a magnetic amplifier. Within a convenient operating range (at a voltage level established by an input, variable transformer), the saturable reactor limits the input voltage to the induction heater so that the power into the effusion cell produces a desired constant temperature.

121-4955

Fig. 8. Block Diagram of Cell-temperature Control System

1. Component Units

The reference signal is supplied by a Leeds and Northrup, M-line Model C-2, low-level set-point unit. The deviation amplifier is a Leeds and Northrup, Model 9834-2, dc-null-detector; the current controller, a Leeds and Northrup, Series 60 Control; and the self-saturating reactor with integral magnetic amplifier, a Leeds and Northrup, 0.8-kVA unit.

The 5-kVA induction-heating generator is a Thermonic, Model 500-A, manufactured by the Taylor-Winfield Corporation, Warren, Ohio. Figure 9 is a schematic diagram of the wiring that permits the use of the small 0.8-kVA saturable reactor to control the 5-kVA heater. The reactor is coupled to the 40-A power line through a transformer capable of carrying the high current. The temperature range within which automatic control is operable amounts to about $\pm 35^\circ$ at a level set by the 240-V, single-phase, two-gang, input, variable transformer.

121-4965

Fig. 9. Schematic Diagram of Controlled Power Supply to Induction Heater

The 1/4-in., water-cooled, copper-tubing conductors that connect the induction-heating generator to the work coil enter the vacuum chamber through a 2-in. flange on the Ultek pump wall. The flanged feed-through consists of a 2-in. Kovar metal-to-glass joint and two small Housekeeper seals, one for each copper tube passing through the glass wall.

2. Operational Notes

Variation of the cell temperature, when held at 836°K over a 12-hr period, amounts to less than 0.2°, as indicated by the monitoring thermocouple attached to the cell.

The effusion cell is grounded through the multiple-lead electrical feed-through and through an rf filter outside the chamber. Without the filter, rectified rf voltage appears on the thermocouple lines as dc off-set potentials that amount to several millivolts.

D. Target-temperature Control System

1. Electronic Control Loops

The method used for maintaining a specified constant target temperature over a 90-min period is shown by the block diagram in Fig. 10.

121-4956

Fig. 10. Block Diagram of Target-temperature Control System

Two interconnected feedback loops are shown. The loop that controls the temperature of the target under study is balanced against a reference loop, which in turn is balanced against a standard (reference) emf.

The unit in the reference loop that is balanced directly against the standard emf is a thermocouple, mounted in a reference target, located in the vacuum chamber close to the experimental test target. The error signal sensed by a null detector is fed

through a deviation amplifier to a circuit controlling the electron gun that heats the reference target. Only enough heat is added to the target to keep the loop in a nulled state.

Concurrently, in the test-target loop an infrared radiometer "looks," via a nodding mirror, into the vacuum chamber through an Irtran-II window (a polycrystalline zinc sulfide material, supplied by Eastman Kodak Co., Rochester, New York), alternately at the test target and at the reference target. The radiance signal from each of the two targets is compared to that of an isothermal black-body cavity inside the radiometer chassis. Each resulting difference signal is processed to appear as a dc potential. These two potentials are bucked against each other, and the difference serves as an error signal, which, when amplified, controls the electron gun that heats the test target. This loop automatically seeks a null condition so that the temperature of the test target equals that

of the reference target. The reference target has, in addition to its controlling thermocouple, a monitoring thermocouple by which its temperature can be displayed on a strip-chart recorder.

2. Check on Fidelity of System

As an independent check on the fidelity of this twin-loop system, which involves the uncertainty of identical emissivities of target surfaces under radiance comparison, a monitoring thermocouple is placed in one of the test targets so that its temperature can also be displayed on a recorder. Hereafter this test target is referred to as the "pilot test target."

3. Developmental Description of System

The target-temperature control system was designed, assembled, and tested at Argonne National Laboratory for the specific application to the molecular-beam experimentation described in this report. Electronics engineer R. N. Lewis did most of the design work; his assistant, L. S. VanLoon, did most of the assembling; and I did most of the final testing that led to necessary "debugging" operations and to the establishment of practical procedures of use. A report of this work has been published separately²⁵ and is reproduced in part as the appendix of this report. A detailed description of the functions of the various components is given, as well as notes on the performance of the system.

E. Thermocouple System

Table IV lists six Chromel-Alumel thermocouple circuits used for measuring and controlling temperature. Each pair of alloyed thermocouple conductors is continuous from the hot junction inside the chamber to the cold junction (pure ice) outside the chamber, except that at a point near the cold junction for each pair, one conductor is intercepted by copper leads for connection to instrumentation. The monitor thermocouples (TC-2, TC-3, and TC-5) are connected through a multiple-station, thermocouple-selector switch to a strip-chart recorder; TC-4 is connected directly to a panel-mounted pyrometer.

TABLE IV. Thermocouple Locations

No.	Location	Function
TC-1	Reference target	Loop control
TC-2	Reference target	Monitor
TC-3	Pilot test target	Monitor
TC-4	Chilled wall in beam system	Monitor
TC-5	Effusion cell	Monitor
TC-6	Effusion cell	Loop control

The 28-gauge Chromel and Alumel conductors are insulated inside the chamber with 2-cm lengths of thin-walled glass tubing. Each pair extends to the outside through a glass-walled feed-through in one of the Ultek flanges. Small holes in the glass wall, through which the wires pass, are made vacuum-tight by applying a film of Torr Seal (a low-vapor-pressure resin, manufactured by Varian Associates, Palo Alto, California) to the outside surface of the glass.

F. Liquid-nitrogen Cooling System

Liquid nitrogen is circulated through the target magazine, through the wall on which the defining orifice is mounted, and through the chill block that faces the effusion cell, by means of a centrifugal pump, purchased from Edwards High Vacuum, Ltd., Manor Royal, Crawley, Sussex, England. The pump, designated as Model 2, Code No. E7701, is especially designed for circulating liquified gases. When the system is cooled to liquid-nitrogen temperature, the liquid is discharged from the return line into a 12-liter, Dewar-flask reservoir. The liquid level in the reservoir is automatically maintained within given limits by an appropriate controller, and makeup nitrogen is supplied from a 50-liter tank.

The chilled components inside the chamber are series connected by flexible, stainless steel hose. Ultek Corporation supplied the feed-throughs that conduct the lines through the flanged ports in the pump wall.

G. Materials

The interacting materials in this molecular-beam study were anhydrous nickel chloride and metallic molybdenum, gold, and nickel. The nickel chloride was prepared by resubliming reagent-grade material in a transpiration apparatus, using dry HCl gas as the carrier. The metal targets were cut from rod stock, sandblasted on one side, polished on the other, cleaned in appropriate solvents, and degassed in the vacuum chamber at 1025°K for 5 min or more.

IV. EXPERIMENTAL PROCEDURES

A. Preparation for Beam Exposures

Ten clean metal targets are rinsed sequentially with 1% H_2SO_4 , distilled water, and reagent-grade acetone; dried rapidly with a heat gun; and mounted in the magazine, which is also thoroughly flushed with water and pure acetone and dried in an oven. The targets are mounted as shown in Fig. 6, each with the polished side facing into the collector cavity. With the tungsten-wire pins secured in their proper positions, it is necessary only to slip the target into position, engage the quartz pins in the target groove, and tighten the setscrew. Before the pilot test target is mounted in the top position, its thermocouple (the leads of which are insulated near the target by a tiny, ceramic duplex conduit) is inserted into a thermocouple well (drilled from the cylindrical side of the target) and secured to its interior by a setscrew. The dangling, glass-insulated leads are secured to the upper portion of the magazine by a few turns of aluminum wire (as shown in Fig. 5).

The 6-in. flanged cover atop the bell jar is removed, and, with dry nitrogen flowing outward, the loaded magazine is lowered into its vertical track and locked into position. The stainless steel, flexible hoses, connecting the magazine to the liquid-nitrogen line, are attached via Conoseal joints (supplied by Aeroquip Corporation), which are then tested for vacuum-tightness by a mass-spectrometer leak detector. The conical-shaped Conoseal gaskets may be reused in these joints several times before replacement is necessary.

The glass-covered thermocouple leads from the pilot test target are connected at the insulated terminals, mounted on the spacer ring in the 6-in. flange. With the output from this thermocouple displayed on the recorder, the magazine is cranked down and up through its entire range to demonstrate the absence of malfunctions, such as shorts in the thermocouple circuit.

A small quantity of Apiezon H grease is applied to the 6-in. O ring, and the flange cover is replaced with three flange bolts lightly tightened. The flow of dry nitrogen into the chamber is shifted from the electron guns (shown in Fig. 3) to the fore-vacuum manifold. The rubber hose is then removed from each glass-tubing gun tail (shown in Fig. 1), and, with a very low-pressure stream of nitrogen flowing out through the gun tail, the latter is softened and sealed off with a glassblower's torch. The nitrogen is shut off, and evacuation of the large vacuum chamber is started by connecting through the fore-vacuum manifold and molecular-sieve trap to the mechanical pump. The bake-out heating tapes are turned on, and the system is left for overnight evacuation and bake-out.

When the pressure in the chamber is reduced to $<10^{-2}$ Torr, the system is leak-tested and the Ultek vac-ion pump is turned on by the procedure given in the manufacturer's instruction manual.

After the pressure in the chamber is reduced to $<5 \times 10^{-7}$ Torr, the electron-gun filaments are turned on and the guns are activated by the procedure given in the appendix.

Each test target is degassed at about 1025°K for at least 5 min by electron-beam heating, the power control for which is provided by a grid-bias adjustment. This preliminary degassing operation may be done at some time before the day of the beam-exposure experiment.

B. Beam-exposure Experiment

To ensure maximum stability in the instrumentation, all systems of the apparatus are turned on an hour or more before experimentation is started.

When activation of the electron guns is completed (i.e., when 5 mA of current will flow from cathode to grid in each gun, across a dc potential of about 50 V), high voltage (16 kV) is applied, and by appropriate grid-bias adjustment of the test-target gun, each target is again heated briefly to redness (about 1025°K).

After the liquid-nitrogen system has attained an equilibrium temperature, as indicated by thermocouple TC-4 in the defining-orifice wall, the control system for the test targets is standardized for each temperature that is to be used in the experiment. To this end, the reference target is heated to temperature T by setting the reference emf on the L&N potentiometer at the appropriate value and adjusting the grid-bias control until a nulled condition in the feedback loop is indicated on the reference-loop null meter (i.e., until the emf of thermocouple TC-2 in the heated reference target is equal and opposite to the reference emf). Then, by manipulation of the grid-bias control on the test-target gun, the temperature of the pilot test target is raised until the null meter in the test-target loop shows that the infrared radiation from the test target is equal to that of the reference target. Next, the output of thermocouple TC-3 in the pilot test target is compared, by display on the recorder, to the output of thermocouple TC-2 in the reference target. If different, they are made to agree by adjusting the potentiometer ρ , shown in Fig. 27. This standardization, which consists of forcing the temperatures of the reference target and pilot test target to be identical when the radiance outputs are identical, is carried out for each temperature to be used in the series of exposures. The potentiometer settings and the corresponding radiometer sensitivities for the set of temperatures are tabulated. A typical set of such data is graphically represented in Fig. 28.

The reproducibility of such a standardization, using the same two targets, say a day later, amounts to temperature differences of about $\pm 1^\circ$ over most of the operating range. At temperatures below about 400°K , where the radiometer error signal (i.e., target radiance to black-body-cavity radiance) becomes quite weak, the reproducibility may be no better than $\pm 10^\circ$. The standardization that is applicable to the pilot test target is assumed to be likewise applicable to each of the other test targets. This assumption is valid only if the emissivity of each test target equals the emissivity of the pilot test target.

With the standardization completed and with all systems stabilized to normal operation, the targets are sequentially exposed to the molecular beam. In each case, the reference target is brought to the desired temperature (as monitored by TC-2) by setting the reference potential on the L&N potentiometer and by adjusting the grid-bias control of the gun until the reference null meter is balanced at zero. The calibration potentiometer is set at the appropriate value, ρ , and the radiometer sensitivity is appropriately adjusted. The test-target null meter is made to balance at zero by adjusting the grid-bias control on the test-target gun. The molecular-beam shutter is opened for a measured time (usually 90 min) and then closed, and the electron beam to the test target is shut off. The magazine is shifted to bring the next target into alignment with the beam; the next temperature is established for the exposure; the molecular-beam shutter is reopened; etc.

When the exposures are completed, all systems are shut down except the vac-ion pump in the high-vacuum chamber. The pump is left in operation while the chamber warms to room temperature.

C. Analysis of Deposits

To relieve the vacuum in the chamber, the Ultek vac-ion pump is shut off and dry nitrogen is admitted slowly through the main shutoff valve from the fore-vacuum manifold, which is previously pressurized at 2 lb. The shutoff valve is cautiously opened, only enough to allow simultaneous flow of nitrogen through two flowmeters: one in the dry-nitrogen line that leads to the fore-vacuum manifold, and the other to a 2-lb relief valve. This arrangement prevents the nitrogen-supply line from being subjected to sudden evacuation by the large chamber, and avoids the buildup of high pressures in the chamber after the vacuum is relieved.

An hour or more is required to increase the pressure in the chamber to 1 atm. During this period, the bake-out heating tapes are turned on for about 15 min to make certain that no internal parts of the chamber are cooler than room temperature when the chamber is opened. This avoids contamination of the NiCl_2 deposits by moisture in the air.

When the pressure in the chamber begins to exceed 1 atm, a vent valve on the fore-vacuum manifold is opened. The flow of dry nitrogen is diverted from the manifold to the two rubber hoses to be connected to the glass-tubing tails on the electron guns (shown in Figs. 1 and 3). The tip of each tail is broken off, and a rubber hose is slipped on. At this stage, dry nitrogen is flowing into the chamber through the two guns, out through the shutoff valve to the manifold, and finally out through the vent valve to the atmosphere.

The flange cover is removed from the top of the chamber, leaving the Viton O ring in place. A sheet of aluminum foil is crimped over the open flange (the 6-in. hole being reopened by tearing away part of the foil) to isolate the greased surfaces of the flange during magazine-removal operations.

The thermocouple leads to TC-3 are disconnected at the terminals on the flange spacer ring, and the liquid-nitrogen hoses are disconnected from the magazine. With a clean, dry, transparent plastic bag (51 x 67 cm) placed over the hole, the magazine is grasped through the bag and drawn upward, out of the chamber, and into the bag, with a minimum of exposure to the moisture of room air. The flange cover is replaced, leaving the stream of dry nitrogen to flow out of the chamber through the manifold vent.

Ten labeled 1-cm spectrophotometer cells, a jeweler's screwdriver, and a pair of Teflon-coated tweezers are placed in the plastic bag with the target magazine. Inside the bag, into which a stream of dry nitrogen is conducted to protect the anhydrous, hygroscopic NiCl_2 deposits from the moisture of the room air, the targets are transferred to the spectrophotometer cells. The cells are tightly closed with rubber caps, which are cut from 1-ml eyedropper squeeze bulbs. The targets are then removed from the bag for microscopic examination through the optically flat walls of the glass cells. If no microscopic study is anticipated, round glass vials with plastic stoppers (pictured in Fig. 5) are more conveniently used for enclosing the targets.

The quantity of NiCl_2 on each target and on each collector is determined by dissolving the deposits in water and analyzing colorimetrically with dimethylglyoxime.⁴⁴ Solution of the deposit on the target is made by transferring the target to a glass funnel that is placed in a 25-ml volumetric flask, and rinsing several times with a stream of water from a plastic wash bottle. The deposit on the collector is also transferred into a 25-ml volumetric flask by directing a stream of water onto the gold-plated walls of the collector. A watertight seal is made at the collector cavity between the flat bottom surface of the horizontally mounted magazine and the flask by means of a short section of rubber tubing that fits over the mouth of the

flask. This rubber-tubing sleeve is held firmly against the under side of the magazine with one hand while the deposit is washed from the collector walls into the flask with the other. After the transfers are completed, all the solutions are acidified by adding a drop of concentrated H_2SO_4 to each flask.

The color of the dimethylglyoxime complex is developed in each flask by the following steps: cool in a tray of ice; add in sequence, with thorough stirring, 10 drops of potassium citrate solution (0.5 g/ml), five drops of concentrated H_2SO_4 , and 10 drops of freshly prepared bromine water; add 3 ml of concentrated NH_4OH solution; add 10 drops of 1% dimethylglyoxime; dilute to volume (25.0 ml); transfer to a 5-cm spectrophotometer cell; and read the optical density at a wavelength of 520 μ .

The average optical density obtained from blank solutions, carried through the same colorimetric procedure, is deducted to give a net optical density, OD, which is proportional to the amount of nickel in solution.⁴⁴ The sticking coefficient, β , is evaluated from the net optical densities produced by nickel dissolved from the target and from the collector as

$$\beta = \frac{\text{OD}_t}{\text{OD}_t + \text{OD}_c} \quad (10)$$

V. EXPERIMENTAL RESULTS

Measurements were made to determine the sticking coefficient, β , of nickel chloride vapor impinging on metal surfaces of molybdenum, gold, and nickel in the range of 80-750°K. This coefficient is considered to be the ratio of the quantity of NiCl_2 that is finally measured on the target at the end of the experiment to the total quantity that strikes the target during the experiment, and may be represented (except where noted) by the experimentally measured ratio of Eq. 10.

A. Molybdenum Targets

Molybdenum targets, prepared from 3/8-in. rod stock, were sand-blasted on one side for radiometric temperature control and polished on the other to a mirror finish for interaction with the molecular beam of NiCl_2 .

1. Beam Exposure of Heated Targets

a. Sticking Coefficient. Figure 11 shows the experimental data obtained in four series of exposures. The sticking-coefficient values are plotted against the temperatures at which the targets were held during the 90-min exposures. Also plotted, as a frame of reference, is the theoretical sticking-coefficient curve, the calculation of which (in Section III.A.3) is based on the geometry of the system and on the vaporization character of nickel chloride.

Although the reproducibility of experimental data is seen to be highest when Series Q is compared to Series R, and Series W to Series Y, all four sets of data show mutual agreement to the extent illustrated in Fig. 12, where all the data are plotted to generate a composite curve.

b. Experimental Data versus Theory. Clearly the composite curve does not agree with the theoretical one. A striking discrepancy appears in the slope with which it descends from the coefficient level of unity to zero. This variation occurs over a temperature span of about 265°, as compared to about 60° for the theoretical curve. Another deviation is in the point at which it intercepts zero, namely, about 35° cooler than that of the theoretical curve.

c. Incident NiCl_2 . Experimental values of total-arrived nickel chloride for Series Q, R, W, and Y are listed in Table V for comparison with the value calculated from the product of the estimated arrival rate (in Table III) and the duration of exposure. The comparison is made on the basis of optical-density units.

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Fig. 11. Sticking Coefficient vs Temperature for Beam Exposure of Heated Molybdenum Targets in Series Q, R, W, and Y. One set of targets was used for Series Q; another set for the eight succeeding series, including R, W, and Y.

Fig. 12

Composite Data for Series Q, R,
W, X, and Y

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TABLE V. Total NiCl_2 Measured on Targets and Collectors for Series Q, R, W, and Y. Optical densities are listed in order of target temperatures, from highest to lowest.

Series	Q		R		W		Y
Day of Experiment	1st	2nd	1st	2nd	1st	2nd	1st
Optical Density	0.091		0.093		0.067		0.095
	0.094		0.091		0.068		0.093
	0.095		0.093		0.075		0.094
	0.102		0.096		0.076		0.097
		0.095	0.091			0.096	0.096
		0.096		0.090		0.099	0.095
		0.094		0.089		0.091	0.098
		0.098		0.097		0.095	0.097
		0.101		0.092		0.100	0.095
		0.102		-		0.086	0.098
Average	0.097 ± 0.004		0.092 ± 0.003		0.085 ± 0.013		0.096 ± 0.002

Calculated value:

$$\begin{aligned}
 \text{Incident NiCl}_2 &= (\text{arrival rate}) (\text{duration of exposure}) \\
 &= (1.68 \times 10^{-11} \text{ mole/sec} \times 1.10 \times 10^6 \text{ OD/mole}) (5400 \text{ sec}) \\
 &= 0.100 \text{ optical density}
 \end{aligned}$$

The factor used for converting moles of nickel to corresponding optical-density units is derived from the average value obtained from 20 analyses of a standard nickel solution containing $4.57 \mu\text{g}$ of nickel per aliquot. These results are shown in Table VI. The relative standard deviation from the mean optical-density value is 2%. The conversion factor is $1.10 \times 10^6 \text{ OD/mole}$.

The experimental values of total-arrived nickel (given in Table V) for Series Q, R, and Y are lower than the calculated amount by 3-8% and have relative standard deviations from the respective means of 2-4%. The agreement of the total NiCl_2 data at a relatively constant level

TABLE VI. Optical-density Measurements on Solutions Containing 4.57 μg of Nickel. Made in conjunction with Experiments P-Z.

Experiment Series	Optical Density
P	0.083 0.084
Q	0.085 0.086
R	0.086 0.086
S	0.083 0.087
T	0.085 0.086
U	0.085 0.084
V	0.087 0.087
W	0.088 0.086
X	0.089
Y	0.087 0.085
Z	0.085

Mean = 0.086 ± 0.0015 S.D.

Relative standard deviation from mean: 2%
Conversion factor:

$$\frac{0.086 \text{ OD}}{4.57 \mu\text{g}} \times 58.7 \times 10^6 \mu\text{g/mole} = 1.10 \times 10^6 \text{ OD/mole}$$

throughout a series (except Series W) indicates that the large variation of sticking coefficient with temperature does not appear to be related to the arrival rate of the NiCl_2 molecules.

In Series W, the values obtained on the first of two days of experimentation were much lower than normal. The cause for this abnormality is unknown. Possible explanations include temporary obstruction in the orifice of the effusion cell or an undetected drop in temperature of the effusion cell.

d. Microscopic Examination. Microscopic examination revealed that the appearance of the deposits was apparently significantly influenced by the grain orientation of the polycrystalline molybdenum at the surface of the target, yet insignificantly influenced by embedded foreign particles of polishing abrasive, and by related pits and scratches.

At a magnification of 100X, the deposit appeared to be a continuous film, yellowish tan in color, and varying in shade according to

zones of irregular boundaries, which corresponded in size to grain boundaries that were discernible on uncoated surfaces of the metal. Figure 13b shows a typical example of a deposit (collected at 480°K; $\beta = 0.49$) in which at least three shades of grey can be distinguished. By direct observation through the microscope, three or more shades were clearly discernible. Under conditions of lower temperatures and correspondingly higher sticking coefficients (>0.75), the yellowish-tan deposit became overlaid with what appeared to be a lavender layer that was less sensitive to the grain orientation of the substrate.

Figure 13a shows the same molybdenum surface (not necessarily the same site) without NiCl_2 deposit. A comparison of the two photographs indicates that the appearance of the deposit is not noticeably affected by surface pits, inclusions, and other irregularities that are large enough to be seen by 100X magnification.

An experiment (Series X) was performed to test further the effect of the surface quality of the target on the sticking coefficient. The cleaned targets were graded as "good" if only two or three surface inclusions were detected in a field of the size (0.7×0.9 mm) shown in Fig. 13a, "fair" if about like Fig. 13a, and "bad" if considerably "dirtier" than Figure 13a. Table VII gives the sticking-coefficient values obtained on

ten targets. They are labeled in the first column and graded in the fourth column. There appeared to be no correlation between sticking coefficient and surface quality at 480 and 500°K. The coefficient values obtained in the 90-min exposures of this experiment are included in the composite graph of Fig. 12.

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1/2 mm

(a) Clean target. Inclusions of abrasive particles and related pits are visible.

(b) Same target with layer of NiCl_2 collected at 480°K. $\beta = 0.49$.

Fig. 13. Photographs of Polished Surface of Molybdenum Target

TABLE VII. Data of Series-X Experiment. Performed to test the dependence of the sticking coefficient on the quality of the surface and on the length of exposure to the molecular beam.

Target No.	Temp, °K	Exposure, min	Surface Grade	Sticking Coefficient
6	500	90	Good	0.48
5	500	90	Fair	0.55
1	500	90	Bad	0.51
10	500	60	Good	0.60
8	500	60	Fair	0.50
4	480	90	Good	0.49
9	480	90	Fair	0.49
7	480	90	Bad	0.65
3	480	60	Good	0.50
2	480	60	Fair	0.52

Under certain conditions, the appearance of the NiCl_2 deposit was remarkably, though not reproducibly, altered by exposure to moisture. In some instances, NiCl_2 -coated targets could stand uncovered for several minutes in the room air without appreciable change in microscopic appearance. In Series W, however, all the deposits apparently became sufficiently contaminated by moisture during transfer from the vacuum chamber to the capped storage ampoules (Section IV.C) that the material recrystallized as hydrates of NiCl_2 , giving microscopic appearances as shown in Fig. 14.

Fig. 14. Photographs of Partially Hydrated Nickel Chloride Deposits

2. Evaporation Experiments

Two experiments (Series U and V) were performed in which each degassed molybdenum target was cooled to near liquid-nitrogen temperature; exposed to the NiCl_2 beam for 90 min; and then, with the NiCl_2 beam off, held at temperature T for 90 min. Figure 15 shows the final distribution of the NiCl_2 that entered the target-collector system, expressed as sticking coefficients on the targets. For comparison, the theoretical curve and the experimental curve generated in Fig. 12, for molybdenum targets exposed at temperature T , are also reproduced.

Fig. 15
Sticking Coefficient vs Temperature for Evaporation of NiCl_2 Previously Deposited at 80°K

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Clearly, these experimental values also form a composite curve that is lower than theoretically expected, yet considerably higher than that obtained from beam exposure of heated targets. The curve is characterized by a zero intercept at $572 \pm 11^\circ\text{K}$ (S.D.), a point about $35 \pm 11^\circ$ below what is expected for the evaporation of NiCl_2 from a surface of crystalline NiCl_2 , and possibly by a slight dip in the region of $400\text{-}450^\circ\text{K}$.

3. Predeposition Experiments

Two other sets of unheated, degassed molybdenum targets (Series T and 2A) were exposed to the NiCl_2 beam, as in the evaporation experiment above, but, instead of thereafter only heating each target for 90 min at temperature T, the shutter was reopened to give an additional 90-min exposure at temperature T. This was, in effect, a combination of the type of experiment that produced the data of Fig. 12 and the evaporation experiment of Fig. 15. Thus, if at every temperature T the amount of nickel that was experimentally expected to be retained on the target in an evaporation experiment is deducted from that of the combination experiment, the remainder should be equivalent to that of Fig. 12.

In Fig. 16, the analytical data for these double exposures, reduced to coefficient form, is plotted on the basis of a single 90-min exposure, so that complete condensation produces a sticking coefficient of 2.0. The resulting experimental curve is labeled 1.

The data of the evaporation experiment (plotted in Fig. 15) are represented in Fig. 16 as curve 2. The difference between the composite curves of the combination experiment and the evaporation experiment, 1-2, is plotted as curve 3. The theoretical curve, 6, and the experimental curve, 4, generated from beam exposures of heated molybdenum targets containing no predeposited material, are also replotted for comparison.

The difference between curves 3 and 4 (i.e., curve 5) represents the apparent enhancement of condensation of nickel chloride on molybdenum metal by the presence of a coating of NiCl_2 (predeposited at 80°K), equivalent in thickness to more than 30 monolayers (as discussed in Section III.A.3).

Fig. 16

Sticking Coefficient vs Temperature for 90-min Beam Exposure of Heated Targets Previously Exposed for 90 min at 80°K; Coefficient Based on Single Exposure

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Figure 17 shows the curve that is generated when the sticking coefficients of Series T are calculated on the basis of a single 180-min exposure. The heated-target composite curve (Fig. 12) and the theoretical curve are again replotted for comparison.

As a test of the effect of the quantity of predeposited NiCl_2 on the enhancement of sticking probability, the above-described experiment was repeated, using a predeposition exposure (at 80°K) of only 3 min (about one monolayer) instead of 90 min. The results of this experiment (Series Z), plotted in Fig. 18, do not verify an appreciable enhancement. The experimental curve coincides closely with that of Series Y (replotted for comparison) in which there was no predeposition.

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Fig. 17. Sticking Coefficient vs Temperature for 90-min Beam Exposure of Heated Targets Previously Exposed for 90 min at 80°K; Coefficient Based on Double Exposure

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Fig. 18. Sticking Coefficient vs Temperature for 90-min Beam Exposure of Heated Targets Previously Exposed for 3 min at 80°K

4. Summary of Results with Molybdenum Targets

Experimental plots of the variation of sticking coefficients with target temperature differed from the theoretically expected curve in shape and in position on the temperature scale. Microscopic examination indicated that the appearance of NiCl_2 deposits on heated targets was influenced by grain orientation of the substrate metal, but not by surface inclusions and imperfections that were visible by 100X magnification. The sticking of NiCl_2 on heated molybdenum metal was enhanced by a 90-min predeposit of NiCl_2 applied when the target was at 80°K.

B. Gold Targets

The procedure for determining sticking coefficients was also applied to two sets of gold targets. Like the molybdenum targets, they were sandblasted on one side and polished on the other. The relatively soft gold was not as highly polished as the molybdenum.

Figure 19 is a composite plot of the experimental points for the two experiments and a reproduction of the theoretical curve and of the composite molybdenum curve for comparison. The gold and molybdenum data appear to coincide, within experimental error, up to about 450°K.

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Fig. 19. Sticking Coefficient vs Temperature for Beam Exposure of Heated Gold Targets

At higher temperatures, the coefficients for gold appear to diverge to lower values and become zero at a point about 50° cooler than for molybdenum.

At the higher temperatures, particularly 600°K and above, a drastic decrease in the total amount of recoverable nickel (target nickel plus collector nickel) was observed for gold targets that was not observed for molybdenum. With one set of gold targets, the subsequent analysis for a 600°K target exposure showed that the

total measurable nickel had dropped to 17% of the average value obtained for targets at lower temperatures, and the analysis for a 700°K target exposure yielded only 9%. The corresponding figures for the other set of gold targets were 68 and 32%.

This decrease in total measurable nickel suggests that some other process was present at elevated temperatures. Such a process might be diffusion of nickel into the gold substrate. Diffusion would account for low results in the measurement of total nickel by the colorimetric procedure, which involves removal of nickel from the metal surface by aqueous

dissolution. Furthermore, diffusion would tend to have a lowering effect on sticking coefficients by depleting the surface of NiCl_2 that otherwise would accumulate for subsequent solution and measurement.

At the higher temperatures, where loss of material by diffusion into gold was suspected, Eq. 10 was modified for the calculation of experimental sticking coefficients (plotted in Fig. 19) by using for the denominator an average of total-arrived nickel, obtained at lower temperatures where no diffusion was suspected.

C. Nickel Targets

Before the use of molybdenum and gold targets, several experiments were performed with degassed nickel targets that were prepared in the same manner as described for molybdenum and gold. This study was complicated, however, by a side reaction that apparently occurred between the deposited NiCl_2 and the nickel substrate in the presence of moisture, before and/or during the removal of the deposit from the target by aqueous dissolution for colorimetric analysis.

When the removal of the deposit was attempted by rinsing or soaking the target with water or ethanol, a dark, amorphous, water-insoluble residue remained on the target in the area previously occupied by the NiCl_2 deposit. This residual material, which adhered tenaciously to the metal surface, was identified, by chemical and physical properties, as Ni(OH)_2 . When its solution in dilute ammonium hydroxide was combined with the solution obtained from washing the target with pure water, subsequent colorimetric analysis showed the total nickel removed from the target to be about twice as much as was deposited by the beam.

In spite of this apparent side reaction, attempts were made to estimate the sticking coefficients of NiCl_2 on nickel targets by using two methods of approximating the amount of NiCl_2 on each target. The first method was to wash the target with water only, to analyze the resulting

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Fig. 20. Sticking Coefficient vs Temperature for Beam Exposure of Heated Nickel Targets; Solution of Deposit by Water Only

solution, and to ignore the insoluble residue remaining on the target (regarded as a corrosion product of the absorbate-substrate interaction). The accuracy of this method apparently varied with the tenacity with which the Ni(OH)_2 clung to the metal substrate during the water wash. Results obtained from three series of exposures, using this method, are shown in Fig. 20. Although the precision is not good, and the accuracy of the data is in doubt, the general form of the sticking-coefficient curves is comparable to that of molybdenum and gold targets.

The second method of approximating the amount of NiCl_2 collected on each nickel target was to wash with both water and dilute ammonium hydroxide and to assume that half the nickel thus put into solution came from deposited NiCl_2 and the other half from corrosion of the substrate. The ob-

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Fig. 21. Sticking Coefficient vs Temperature for Beam Exposure of Heated Nickel Targets; Solution of Deposit by Water and Dilute NH_4OH

vious uncertainty that characterized this procedure was the assumption that all the deposited NiCl_2 entered into a quantitative one-to-one reaction with metallic nickel in the presence of water. Nevertheless, the results obtained on three series of exposures that were analyzed by this method were in good mutual agreement (as shown in Fig. 21) and produced a composite curve for the sticking coefficient that does not differ greatly from that of molybdenum.

D. Sticking Coefficient versus Length of Exposure

In a series of exposures of nickel targets, each at 517°K , the duration of exposure was varied from 0.25 to 3 hr. The amounts of NiCl_2 found on the collectors (unaffected by the side-reaction interference to determination of target nickel) are plotted in Fig. 22. The apparent linear variation indicates that the sticking coefficient, about 0.5, was constant for the series and was independent of the length of exposure, at least under the experimental conditions that applied in this investigation. The stray point in Fig. 22 for the 2-hr exposure coincided with an abnormal experimental condition of a temporary build-up of pressure in the vacuum chamber, due to inadvertent depletion of liquid nitrogen in the chilling system.

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Fig. 22. Variation of Amount of NiCl_2 on Collector with Duration of Beam Exposure

In another experiment, five molybdenum targets were exposed at 500°K , and five more at 480°K . Three targets in each temperature group were exposed for 90 min and two for 60 min. The resulting analytical data given in Table VII revealed no dependence of the sticking coefficient on the length of exposure.

E. Effect of Degassing Targets

New targets that were heated only briefly to redness (about 1025°K) to remove surface contaminants behaved markedly differently in the usual

exposure procedure from targets that were annealed at this temperature for 5 min or more. The data presented in Fig. 23 were taken from a series of exposures of insufficiently degassed molybdenum targets. In this graph, the

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Fig. 23. Distribution of NiCl_2 in Target-Collector System with Insufficiently Degassed Heated Targets

optical-density measurements of the target nickel and the collector nickel are normalized to the highest total nickel of the series. The difference between this value and each of the other sums of target nickel and collector nickel is plotted as unaccounted-for nickel.

When sufficiently degassed molybdenum targets were used, no perceptible drop in collector nickel, with the corresponding unaccounted-for loss, was observed in the higher temperature range. On the basis of these observations, the dip in the

collector curve can almost certainly be attributed to interference in the deposition of NiCl_2 on the collector by the degassing process of the metal targets. The effect was greatest at about 600°K. At higher temperatures, the target apparently became degassed sufficiently during the exposure to offer diminished interference to NiCl_2 condensation on the collector.

The data reported in Sections V.A-C were obtained with targets sufficiently degassed to show no such interference in the condensation of NiCl_2 on the collectors.

F. Effect of Nonuniformity of Targets

Some of the scatter in the experimental data may be relatable to some property of the individual targets that in two or more experiments tended to vary from one to another in the same relative fashion. For example, in Series Y and Z (shown in Figs. 11 and 18), the data points that seem to be low, with respect to the others, were taken from analyses of the same two targets.

A property that could vary from one target to another within a given experiment and could vary in the same, or different, relative fashion from one experiment to another is the emissivity of the sandblasted surface. Small differences in emissivity between the test targets and the pilot test target correspond to errors in the estimation of target temperature. When present, such differences may prevail from one experiment to another and may gradually change with continued reuse that involves exposures to the atmosphere, to cleaning solvents, to bake-out, and the electron-beam heating.

A method is cited in Section 2.a of the appendix for comparing the relative emissivities of the targets at bake-out temperatures of about 375-425°K. In this temperature range, the radiometer signals are relatively weak so that emissivity differences are not as pronounced as they might be at the higher temperatures of experimentation. However, since no more sensitive test was available, the targets were considered to have identical emissivities if the error in ρ (as discussed in Section 2.a of the appendix) was no greater than ± 0.002 . The experimental results presented in this report are based on the assumption that the emissivities of all test targets were identical to that of the pilot test target.

Another property that varies from target to target, yet apparently does not significantly affect the final results, is the condition of the polished surface that faces the molecular beam, with respect to solid inclusions, pits, and scratches, as discussed in Section V.A.1.d.

VI. DISCUSSION OF RESULTS

The experimental results reported in Section V raise a number of points for discussion. They have indicated that (1) the sticking probabilities of NiCl_2 molecules impinging on a molybdenum metal surface at 350-600°K are considerably less than would be expected for equilibrium at a target of crystalline NiCl_2 , (2) the predeposition of NiCl_2 on the metal surface at 80°K enhances the sticking probability of subsequent deposition in the range 400-550°K, (3) the sticking probability does not vary appreciably with duration of beam exposure, under the conditions of experimentation, (4) solid-impurity inclusions and related pits and scratches in the metal surface, visible at 100X magnification, have a negligible effect on the sticking probability, (5) the shade of color of the deposited film of NiCl_2 on the metal target is evidently strongly influenced by the grain orientation of the substrate, and (6) when gold targets are used, the total amount of measurable nickel chloride on the target and on the collector is a small fraction of the amount incident to the system for target temperatures above 600°K.

A. Evaporation Data versus Theoretical Curve

The experiment that might have been expected to yield sticking coefficients that coincide most closely with the theoretically calculated values for the range 80-625°K is the evaporation of a film of NiCl_2 previously deposited on the target at about 80°K (as discussed in Section V.A.2).

The amount of nickel chloride expected to be deposited on 80° targets during 90 min of exposure to the beam is

$$D = Z' t = 9.07 \times 10^{-8} \text{ moles}, \quad (11)$$

where Z' is the arrival rate (given in Table III), and t is the time in seconds. The amount of nickel chloride expected to be evaporated from each target at temperature T during 90 min of heating is

$$E = Z'' t = 15.7 p_2 T_2^{-1/2} \text{ moles}, \quad (12)$$

where Z'' is the departure rate (from Eq. 8), and t is the time in seconds. The expected coefficient for the evaporation experiment is, therefore,

$$\beta = \frac{D - E}{E} = \frac{Z' - Z''}{Z'}. \quad (13)$$

(Equation 13 is identical to Eq. 9.)

The experimental data plotted in Fig. 15 indicate that the sticking coefficient may be about 2-5% low and somewhat variable in the range of 400-525°K, and that it drops to zero at $572 \pm 11^\circ\text{K}$, a point that is $35 \pm 11^\circ$ cooler than the zero intercept of the theoretically calculated coefficient.

1. Zero Intercept

The apparent discrepancy between the experimental and theoretical zero intercepts may be considered to be attributable to an experimental condition or to some phenomenological character of the heterogeneous system.

One experimental condition to examine is the inadvertent overshooting of the desired target temperature that occurred when the target was heated from 80 to $T^{\circ}\text{K}$ at the beginning of the 90-min evaporation period. During warmup, the temperature of the target could not be monitored until it almost reached the value at which it was automatically controlled. Consequently, it was easy to overshoot a few degrees (say, 1-25°) for about 30 sec, depending on the amount of compensation allowed by manual control of the gun-bias adjustment. Such brief overshoots would probably not cause the NiCl_2 deposits to evaporate so completely as to make the experimental curve intercept zero at a temperature 35° too low. According to the discussion on page 53, the time required for the evaporation of a 90-min deposit at a temperature near 600°K should be of the order of 90 min, not a few seconds. Hence, the discrepancy between the experimental curve and the theoretical curve in the position on the temperature scale must be attributed to some other cause.

Another possible source of experimental error is that all the coefficient values were slightly shifted on the temperature scale because of a poor match in emissivity between the pilot test target (on which the preexperiment standardization of radiance is based) and all the other test targets. Although the possibility of such an error cannot be ruled out, it is considered to be unlikely because the pilot test target and the other test targets were prepared and cleaned at all times in the same way. The pilot test target and the other test targets appeared to have the same emissivity when checked by the radiometer during bake-out of the chamber (discussed in Section 2.a of the appendix). Furthermore, two different pilot targets were used for the two evaporation experiments represented in Fig. 15, and in both experiments values near zero were obtained at temperatures about 40° below the temperature of the theoretical-curve intercept.

A more likely experimental cause for a temperature shift is the possible failure of the thermocouple in the pilot test target to accurately represent the temperature of the target. The flow of heat through the leads of the thermocouple, which is secured to the bottom of the thermocouple well by a setscrew, to the environment of liquid-nitrogen-cooled surfaces outside the well may have caused the temperature of the thermocouple to be a few degrees lower than that of the target.

If the displacement of the zero shift is not altogether due to experimental error, the apparent increase in vapor pressure of NiCl_2 in these experiments over that of NiCl_2 in an equilibrium system may be attributable to some fundamental character of the solid condensate-substrate

system. One phenomenological situation that might be considered to explain a reduced energy of vaporization is that lattice strains are present in the thin crystallites of NiCl_2 , due to a mismatch of lattices at the interface between the nonmetallic crystalline NiCl_2 and the metallic crystalline substrate.⁵³ Another phenomenon to consider is that the NiCl_2 deposited at 80°K is in an amorphous form of higher vapor pressure than that of crystalline NiCl_2 , and that the warmup time from 80°K to the approximate range of $575^\circ\text{K} < T < 605^\circ\text{K}$ is so brief that an insignificant fraction of the condensate is converted to the more stable, crystalline form before the major part is vaporized. Indeed both situations might also be considered to apply to some extent. However, in either case, the heat of formation of the less stable form, if such exists, has to be of the order of a kilocalorie greater than that of bulk crystalline NiCl_2 to produce a theoretical curve that coincides with the experimental curve in Fig. 15 (a requirement which, at this point, places some doubt on this interpretation).

2. Low Coefficients at Lower Temperatures

The tendency toward low coefficients at temperatures above about 400°K seems to be real and may be related to the physical nature of the 80° deposit of NiCl_2 . Some sort of decrepitation of loosely cohered particles of condensate may be involved during warmup to temperature T . Actually, no completely satisfactory explanation seems to be evident at this point.

Although the slight dip in the generally low experimental curve at about 450°K appeared to be evident in both experiments, the significance of the dip is somewhat uncertain due to the 2% uncertainty in nickel measurements (given in Table VI).

B. Condensation Data versus Theoretical Curve

Since deviation from ideal behavior was observed in the evaporation experiments (as discussed in Section A above), some deviation might be expected also in the condensation experiments in which the molecular beam impinged for 90 min on initially clean metal targets at temperature T . The greater extent of deviation, demonstrated in Figs. 11 and 12, was unexpected, however, and warrants further discussion.

1. Reduced Slope of Curve

The results of the heated-target condensation experiments differ most from those of the evaporation experiments in the slope of the coefficient-temperature curve. For, whereas both the theoretical curve and

the composite evaporation curve of Fig. 15 drop from their maximum levels to zero within a temperature span of about 60° , the composite heated-target curve of Fig. 12 drops over a span of about 265° .

Before choice of explanations is offered for the drastically reduced slope, other pertinent experimental observations, reported in Section V, should be listed. They are: (1) Of the two gaseous-movement rates involved, namely, arrival rate to the target-collector system and departure rate from the target, only the latter is to be considered for nonideal behavior, because the former is generally constant under the conditions of the experiments (as discussed in Section V.A.1.c); (2) the sticking coefficient is apparently enhanced for heated targets when such targets are precoated with NiCl_2 by exposure at 80°K to a NiCl_2 beam for 90 min, but not when precoated for only 3 min (Section V.A.3); and (3) the sticking coefficient appears to be independent of the length of exposure (Section V.D).

One explanation that might be considered for the low sticking coefficients over the range of $300\text{--}570^\circ\text{K}$ is that the temperature of the outer molecular layer of NiCl_2 , condensed on the target, is higher than that of the target. The argument might be made that, due to the relatively low thermal conductivity of a film of NiCl_2 , the drain of heat from the outer molecular layer (which is receiving energy from condensation of beam molecules) to the metal substrate is slow enough to permit a temperature gradient across the film sufficiently large to lower the sticking coefficient.

This explanation seems to conflict with three other considerations. First, if a temperature gradient across the film were responsible for the low sticking coefficients, then a predeposit of NiCl_2 on the target at the beginning of the heated-target exposure should reduce the coefficient even further. On the contrary, predeposition resulted in enhancement of the coefficient (as discussed in Section V.A.3). Second, the sticking coefficient should vary inversely with the duration of exposure, because the thicker the film, the greater the temperature gradient. But two experiments reported in Section V.D showed that under the conditions of experimentation, the coefficient does not vary appreciably with length of exposure. Third, the heat loss from the outer layer of the deposit to the 80° surroundings by radiation is sufficiently great, compared to the heat added by condensation, that if heat conduction through the film were a reasonable basis for assuming a temperature gradient, the outer layer would indeed be colder rather than warmer than the substrate.

An explanation for the drastically lowered sticking coefficients, which seems to be in harmony with other experimental observations, is that sticking is a net result of at least two competing processes on the surface of the target. One is the growth of crystallites of solid NiCl_2 , in which form the NiCl_2 is retained to produce the observed sticking-coefficient values, and the other is reevaporation from the metal-target surface to the surrounding collector. The rate of sticking, therefore, depends upon the rate

of accumulation in crystallites. The rate of accumulation depends upon the number of growing crystallites, which in turn is governed by the number of nucleation sites. The number of nucleation sites is evidently a function of temperature, but not of the duration of exposure (under the conditions of experimentation).

Thus when a clean metal target at temperature T is exposed to a beam of NiCl_2 molecules, an equilibrium number of nucleation sites, characteristic of temperature T , are established during the first small fraction of exposure time (not defined by this investigation). This population of sites, which remains essentially constant for the remaining duration of exposure, determines the rate at which fixation occurs for the exposure as a whole. Since, after initial establishment, the population of sites does not change appreciably with time, the sticking coefficient does not appear to vary with time.

The population of nucleation sites apparently varies inversely with the temperature of the target, so that the lower the temperature, the greater the number of sites and the higher the sticking coefficients.

This interpretation is expressed within the framework of currently accepted nucleation theory (given in Section II.E). It does not conflict with the mathematical expressions for the rate of nucleation by either the classical^{18,37} or the statistical^{45,46} theory.

If by some means the number of sites should be increased beyond the equilibrium number (characteristic of temperature T), the growth rate might be expected to be correspondingly increased, resulting in a higher sticking coefficient. It may be considered that this supplemental increase of sites was provided in the 90-min predeposition experiment, illustrated in Fig. 16, where the coefficient variation with temperature is plotted for heated-target exposures with and without a predeposited film in curves 3 and 4, respectively. The difference between the two, plotted as curve 5, may be said to represent the extent of enhancement of nucleation on the metal surface by independently providing an excess of NiCl_2 nucleation sites.

It might be asked at this point why the 3-min, 80°K preexposure for Series Z (plotted in Fig. 18) did not provide a measurable enhancement as did the 90-min preexposure. The quantity of material deposited in 3 min, which was equivalent to about one monomolecular layer, may not have been sufficient to survive the rise in the target temperature to T without being substantially lost by evaporation from the amorphous form, before a significant population of stable crystallites could become firmly established on the surface by nucleation.

There is some evidence that the density of nucleation sites also depends on the atomic condition of the metal surface. It was pointed out in

Section V.A.1 that the reproducibility of experimental data obtained in heated-target exposures was best when Series Q was compared to Series R, and Series W to Series Y. The plots of data in Fig. 11 suggest that some enhancement to sticking may be evident in Series W and Y, as compared to Series Q and R; i.e., the data curves of the former show a slight bulge when compared to those of the latter. About the only obvious change in the targets that occurred during the interval between experiments R and W was their reuse for the intervening experiments, Series S, T, U, and V, which involved several 5-min degassing treatments at 1025°K. If indeed there was enhancement, these treatments may have progressively annealed the metal so that on an atomic scale the surface became more conducive to the formation of nucleation sites for a given temperature.

2. Zero Intercept of Sticking-coefficient Curve

The composite experimental-data curve for the heated-target experiments, Series Q, R, W, X, and Y, shown in Fig. 12, intercepts zero at about 570°K, whereas the theoretical curve intercepts it at about 605°K. As indicated by the log p scale in Fig. 7, this temperature difference corresponds roughly to a difference in the vapor pressure of NiCl_2 of about a factor of 10.

Three explanations might be considered for this disparity. One is that the controlling thermocouple in the pilot test target was at a lower temperature than the target. The possibility and consequence of such an experimental uncertainty was discussed in Section VI.A.1 in connection with the evaporation experiments.

A second explanation, also discussed in Section VI.A.1, is that the increase in beam pressure that is required for sticking might be considered to be equivalent to the difference between the vapor pressures of bulk crystalline NiCl_2 and strained, thin-layer deposits of NiCl_2 that are bonded to metal substrates.

A third explanation is that at the higher temperatures the beam molecules are not completely thermally accommodated. That is, one might expect that the thermal accommodation coefficient is less than unity at temperatures $\geq 570^\circ\text{K}$, and that this might partially account for the zero sticking probability between 570 and 605°K. For, if it is considered that beam molecules at an average temperature of 836°K strike a target at 570°K and reevaporate with an average temperature of 605°K, then the accommodation coefficient can be estimated as

$$\alpha = \frac{836 - 605}{836 - 570} = 0.87.$$

One difficulty with this explanation is that the disparity between the experimental and theoretical intercepts for the evaporation experiments (plotted in Fig. 15) is, within experimental error, about the same

as for the condensation experiments, although in the evaporation experiments no thermal accommodation was involved. Nevertheless, if incomplete thermal accommodation is at least partially responsible for the shift of the zero intercept, then one might suspect that internal energy of the triatomic molecule is significantly involved. Accordingly, it might be of interest to test the corresponding behavior of a monatomic vapor such as cadmium or zinc.

3. Complete Sticking at Temperatures $\leq 300^\circ\text{K}$

Essentially all beam molecules that strike the metal target below about 300°K are retained on the target. The plot of curve 3 in Fig. 16 indicates that even a 90-min predeposit (equivalent to 30 or more monolayers) has a negligible effect on the sticking probability below about 375°K . This may imply that nucleation is not essential to sticking below 375°K and that the condensed film is not necessarily in a crystalline form but rather, as discussed in Section VI.A.1, may be amorphous.

4. Microscopic Appearance of Deposit

The apparent influence of the grain orientation of polycrystalline molybdenum (discussed in Section V.A.1) on the shade of color of the yellowish-tan deposit suggests that there was a corresponding influence on the density and/or size of crystallites that were too small to be resolved by 400X magnification. It was not possible to demonstrate, by use of equipment immediately available, that the NiCl_2 concentration was greater on deep-colored grain-defined areas than on light-colored grain-defined areas. Perhaps further information could be gained in this regard by using microprobe analysis of the individual substrate grain faces, or by examining the deposit by electron microscopy.

An indirect indication that substrate grain orientation did influence the rate of condensation (probably by defining the number of nucleation sites for a given temperature) is that relatively large surface imperfections, such as scratches, pits, and inclusions of foreign particles, showed no appreciable effect on either the appearance of the deposit or on the sticking probability (see Fig. 13 and Table VII). Conversely, it may be implied that since substrate grain orientation did apparently affect the depth of color of the deposit, grain orientation also affected the probability of sticking.

C. Proposed Reactions

In accord with the experimental observations described in Section V and the discussions of Sections VI.A and VI.B, a group of reactions are proposed below to represent the processes involved in the evaporation experiments and in the experiments in which initially clean molybdenum targets, at temperature T , were exposed to the NiCl_2 beam.

1. Evaporation Experiments

1. NiCl_2 (s, amorphous, T_S) $\rightarrow$ NiCl_2 (g, T_S)
2. NiCl_2 (s, amorphous, T_S) $\rightarrow$ NiCl_2 (adsorbed, T_S)
3. NiCl_2 (s, amorphous, T_S) $\rightarrow$ NiCl_2 (s, crystalline, T_S)
4. NiCl_2 (adsorbed, T_S) $\rightarrow$ NiCl_2 (g, T_S)
5. NiCl_2 (adsorbed, T_S) $\rightarrow$ NiCl_2 (s, crystalline, T_S)
6. NiCl_2 (s, crystalline, T_S) $\rightarrow$ NiCl_2 (g, T_S)

2. Condensation-Evaporation Experiments

7. NiCl_2 (beam, T_I) $\rightarrow$ NiCl_2 (adsorbed, T_A)
8. NiCl_2 (adsorbed, T_A) $\rightleftharpoons n$ NiCl_2 -nuclei (s, T_S),
where $n = n(T_S)$
9. NiCl_2 (adsorbed, T_A) $\xrightarrow{r_5}$ NiCl_2 (s, crystalline, T_S),
where $r_5 = r_5(n)$
10. NiCl_2 (adsorbed, T_A) $\rightarrow$ NiCl_2 (g, T_A)
11. NiCl_2 (adsorbed, T_A) $\rightarrow$ NiCl_2 (s, amorphous, T_S),
where $T_S \approx 300^\circ\text{K}$
6. NiCl_2 (s, crystalline, T_S) $\rightarrow$ NiCl_2 (g, T_S)
1. NiCl_2 (s, amorphous, T_S) $\rightarrow$ NiCl_2 (g, T_S)

Reaction 8 is written to show that a certain amount of the incoming NiCl_2 molecules is required to establish n critical-sized NiCl_2 nuclei for subsequent growth into crystallites, n being a function of the target temperature. Reaction 9, the rate of which is a function of the number of critical-sized nuclei (or later, crystallites), is the rate-determining reaction in the sticking of NiCl_2 on the target for subsequent measurement.

VII. CONCLUSIONS

Sticking coefficients of nickel chloride on polycrystalline molybdenum, gold, and nickel have been measured by exposing the metal targets, over a range of 80-750°K, to a molecular beam of NiCl_2 at 836°K. Each target, heated to a constant temperature by a radiometer-controlled electron gun, was enclosed in a liquid-nitrogen-cooled collector for the capture of molecules reevaporated from the heated surface.

The experimental coefficient-versus-temperature curve differed drastically from the corresponding theoretical curve calculated on the basis of the equilibrium vapor pressure of $\text{NiCl}_2(\text{s})$ at temperature T , and on the basis of the geometry of the beam. Whereas the theoretical coefficient changed from near unity to zero over a span of about 60°, the experimental coefficient made the transition much more gradually over a span of about 265°.

This observation, along with three other observations, namely, (1) that the coefficient was apparently enhanced by a thin coating of NiCl_2 pre-deposited at 80°K, (2) that the coefficient did not appear to vary with duration of exposure, and (3) that the coefficient seemed to be sensitive to the atomic character of the metal surface, gives support to nucleation theory, which incorporates the following processes: (1) The NiCl_2 -beam molecules, impinging upon the metal surface at temperature T , condense (where T is within a range that theoretically permits net condensation) and become temporarily adsorbed to the metal; (2) some such molecules reevaporate; (3) concurrently, other such molecules move together to form nucleation sites for subsequent formation and growth of crystallites, the equilibrium density of which is a function of temperature; and (4) thereafter, the molecules that do not reevaporate move to such sites and become arrested in crystallite growth. Sticking, thus limited by the temperature-controlled concentration of nucleation sites, is characterized by coefficients considerably lower than would be expected for condensation on crystalline NiCl_2 .

Thin "films" of $\text{NiCl}_2(\text{s})$, deposited on polycrystalline molybdenum at 80°K, appeared to exhibit higher vapor pressures than is characteristic of bulk crystalline NiCl_2 over the range of about 400-600°K. The apparent variance may be explainable by a systematic error in target-temperature measurement and/or by the assumption of an amorphous form of $\text{NiCl}_2(\text{s})$ at the lower temperatures and of a strained-lattice structure in thin crystallites at the higher temperatures. The implied increased heats of formation of the two unstable forms over that of annealed bulk NiCl_2 crystals (~1 kcal) casts some doubt on the latter interpretation.

Investigation of the sticking coefficient of NiCl_2 on gold targets was hampered by what appeared to be diffusion into the metal substrate. Study of the condensation of NiCl_2 on nickel-metal targets was complicated by interference of nickel analysis by an apparent side reaction between the accumulated NiCl_2 deposit and the nickel substrate in the presence of water, resulting in corrosion of the substrate during the analysis.

APPENDIX

Developmental Description and Use of
Target-temperature Control System

The material included in this appendix has been published, in part, elsewhere²⁵ and is added here as a supplement to Section III.D.

1. Description of System

The following paragraphs describe the component parts of the system, particular emphasis being given to newly developed components and to modifications that were made on purchased items in order to meet specific requirements of the molecular-beam experimentation.

a. The Electron Guns

The electron guns are a modified Type 5XP, purchased from Superior Electronics Co., Clifton, New Jersey, at \$15 each. Specified modifications provided by the manufacturer include the placement of the gun elements on a Kovar lead-glass stem to facilitate glass-to-metal seals on the vacuum chamber and the enlargement of all orifices in the gun, except the one nearest the cathode, to 0.070-in. diameter. The orifice enlargement increased the diameter of the beam, yielding a beam current in excess of 1 mA, or a maximum power of about 15 W for target heating.

A modification that accompanies the installation of each gun is the enclosure of the gun elements within a stainless steel tube $6\frac{1}{2}$ in. long,

$1\frac{3}{4}$ in. in diameter, and $1/32$ in. thick (as shown in Fig. 1). Being in floating contact with the spring spacers of the gun, this metal enclosure shields the electron beam from nearby glass walls, which otherwise become charged insulators.

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Fig. 24. Activation Circuit for Electron Guns

The guns are activated initially and then periodically as required. The circuit for activation was built into the system and is shown in Fig. 24. Activation proceeds as follows:

- 1) With the ACTIVATE-OPERATE switch in the ACTIVATE position, the heater voltage is set at about 5 V.

2) The heater voltage is increased in $1/2$ -V steps until grid current is observed on the meter.

3) Over a period of about 10 min, the heater voltage is adjusted in small amounts (up or down) until a final grid current of 5 mA is obtained. The heater voltage is then left at this value.

4) Successive activations of the guns may require increasing values of heater voltage.

The gun supply voltages are obtained in a conventional manner, although the entire supply must "float" at about -15 kV. The components are housed in a corona-free structure with insulated shafts provided to allow adjustments from the front panel. The circuit is shown in Fig. 25. Signal voltages of ± 10 V at the input grids of the NU131 control tubes turn the electron beams from full on to full off.

b. Reference-target Temperature-control System

Figure 26 is a schematic drawing of the reference-target temperature-control system. There are two thermocouples on the reference target: one for use in the feedback-control loop, and one for a continuous record of the temperature. The error meter indicates that a selected temperature has been reached when it hunts about zero.

c. The Radiometer

A Barnes Engineering Model R-4D1 radiometer was chosen for the project because it uses front-surface reflecting optics and a thermistor-bolometer detector. This combination uses all wavelengths of the infrared energy between 1.8 and $25\ \mu$. A mechanical chopper causes the detector to alternately see the external target and an internal black-body reference cavity. Although the radiometer contains circuits for the phase detection of the signal, we chose to use the undetected signal, which appears as a 90-Hz square wave. (The main reason for this decision is discussed in Section 1.e below.)

d. Test-target Temperature-control Loop

The test-target control system is shown schematically in Fig. 27. An oscillator and power amplifier magnetically drive the torsionally suspended nodding mirror at about 10 Hz. The mirror-position pickoff signal is amplified by A3 and used to drive the phase-detector relay, Ry-1. The output of A3 (waveform A of Fig. 27) is diode-coupled to A-4 to yield an output from A-4 of a positive pulse for each mirror transition (waveform B). This pulse trips the monostable, which in turn drives the gating relay, Ry-2. This causes the detector-integrators to process the signals from each target for an identical time interval, regardless of small time differences caused by mechanical changes in the mirror drive and suspension system.

Fig. 25
Circuit Diagram of Electron Guns

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Fig. 26. Temperature-control System for Reference Target

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Fig. 27. Temperature-control System for Test Target

When the nodding mirror is aimed at the test target, the radiometer signal is switched to the positive detector-integrator by Ry-1, and for the reference target to the negative detector-integrator. For identical temperatures of targets with identical emissivities, the positive and negative signals will be equal, and with the potentiometer dial, ρ , set to 0.500, a zero output signal will result. If the reference target is hotter than the test target, a negative output signal will result, and, if cooler, a positive output signal will result. This signal, when amplified and applied to the test-target electron gun, will cause a null condition to exist. The error meter is useful for determining that equilibrium conditions have been established.

e. Emissivity Correction

In Fig. 27, if the two signals S_T (test-target signal) and S_R (reference-target signal) are unequal while the temperatures of the reference and test targets are identical, the potentiometer can be adjusted for a zero output as read on the error meter. We have, for a null,

$$\left. \begin{aligned} \frac{S_T}{\rho} &= \frac{S_R}{1 - \rho} \\ \text{and} \\ \frac{S_T}{S_R} &= \frac{\rho}{1 - \rho} \end{aligned} \right\} \quad (14)$$

The Stephan-Boltzmann Law states that the radiance from a target radiating in a cosine or Lambert fashion is

$$H_T = \frac{\sigma T_T^4 \epsilon_T}{\pi}, \quad (15)$$

where

σ = Stephan-Boltzmann constant,

T_T = temperature of the target in $^{\circ}\text{K}$,

and

ϵ_T = emissivity of the target.

The signal due to chopping is

$$S_T = H_T - H_C, \quad (16)$$

where H_C is the radiance from the reference cavity in the radiometer head, the emissivity of which is taken as unity. If Eq. 15 is applied, Eq. 16 yields

$$S_T = \frac{\sigma T_T^4 \epsilon_T}{\pi} - \frac{\sigma T_C^4}{\pi} \quad (17)$$

Similarly, the signal obtained when observing the reference target is

$$S_R = \frac{\sigma T_R^4 \epsilon_R}{\pi} - \frac{\sigma T_C^4}{\pi} \quad (18)$$

The test-target temperature-control system acts to make $S_T = S_R$, or

$$T_T^4 \epsilon_T = T_R^4 \epsilon_R \quad (19)$$

and if $\epsilon_T = \epsilon_R$, the two temperatures are equal. If $\epsilon_T \neq \epsilon_R$, a correction must be made.

During initial pumpdown, it is advantageous to bake out the vacuum chamber. During bake-out, all targets within the chamber are brought to essentially the same temperature. For a bake-out temperature $T_B(1)$, we have, using Eqs. 17 and 18,

$$\left. \begin{aligned} S_T(1) &= \frac{\sigma T_B^4(1) \epsilon_T}{\pi} - \frac{\sigma T_C^4(1)}{\pi} \\ \text{and} \\ S_R(1) &= \frac{\sigma T_B^4(1) \epsilon_R}{\pi} - \frac{\sigma T_C^4(1)}{\pi} \end{aligned} \right\} \quad (20)$$

By adjusting the potentiometer, we can take the ratio of these two signals, i.e.,

$$\frac{S_T(1)}{S_R(1)} = \frac{\rho(1)}{1 - \rho(1)} = \frac{T_B^4(1) \epsilon_T - T_C^4(1)}{T_B^4(1) \epsilon_R - T_C^4(1)} \quad (21)$$

Equation 21 can be rearranged to yield

$$\frac{\rho(1)}{1 - \rho(1)} = \frac{\epsilon_T - \left(\frac{T_C(1)}{T_B(1)} \right)^4}{\epsilon_R - \left(\frac{T_C(1)}{T_B(1)} \right)^4} \quad (22)$$

Similarly, for a second bake-out temperature, $T_B(2)$, we have

$$\frac{S_T(2)}{S_R(2)} = \frac{\rho(2)}{1 - \rho(2)} = \frac{\epsilon_T - \left(\frac{T_C(2)}{T_B(2)}\right)^4}{\epsilon_R - \left(\frac{T_C(2)}{T_B(2)}\right)^4}. \quad (23)$$

If it is assumed that the emissivities do not vary appreciably with temperature, there is now sufficient information to determine ϵ_T and ϵ_R , using the two simultaneous Eqs. 22 and 23. With these values obtained, the proper setting for any given temperatures T_X and T_C can be determined. This is, solving Eq. 22 for ρ ,

$$\rho(X) = \frac{\epsilon_T - \left(\frac{T_C}{T_X}\right)^4}{\epsilon_R + \epsilon_T - 2\left(\frac{T_C}{T_X}\right)^4}. \quad (24)$$

2. Operational Notes

Some information on the practical application of this controlled heating system, gathered after its installation and "debugging," is presented here.

a. Uniformity of Surface Emissivity

In a set of ten test targets, the magnitude of the signal S_T , produced by the radiometer for each target at temperature T , is related to its emissivity by Eq. 17. Equation 24 can be used to show that in comparing two test targets (a and b) to the reference target (T_X , T_C , and ϵ_R being constant),

$$\rho(X)_a = \rho(X)_b$$

if

$$\epsilon_{T_c} = \epsilon_{T_b}.$$

Hence the uniformity of emissivities from one test target to another can be checked by observing the constancy of the potentiometer reading, ρ , at some chamber bake-out temperature, T , as the test targets are moved successively into position for comparison with the reference target.

Table VIII shows a typical set of ρ values obtained on sand-blasted nickel targets at a bake-out temperature of 146°C. It was deter-

TABLE VIII. Typical Potentiometer Readings on a Set of Sandblasted Nickel Test Targets at 146°C

Target No.	Potentiometer Reading, ρ
1	0.499
2	0.502
3	0.501
4	0.500
5	0.505
6	0.500
7	0.502
8	0.501
9	0.501
10	0.502
Average 0.501 ± 0.002	

mined that an error of ± 0.001 in ρ corresponds to a temperature error of about $\pm 0.2^\circ$ at 100°C and about $\pm 0.6^\circ$ at 500°C.

b. Effective Emissivity Difference

Sandblasting of the target surface to a uniform rough texture proved to be an effective method of greatly reducing emissivity differences among test targets, as well as between test targets and the reference target.

An "effective emissivity" difference that

could not be ignored remained, however, between the test target and the reference target. The geometric arrangement of the targets is such that the reference target, located about 0.5 cm in front of the test target and enough to one side that it eclipses about one-fourth of the radiometer's "view" of the test target, radiates only its own emitted energy to the radiometer; the test target behind it not only radiates its own emitted energy but also reflects a significant fraction of energy from the back side of the reference target. This condition causes the radiated signals from the two targets of identical surface texture to be equal only when $T_R > T_T$. The error in the estimate of T_T (i.e., $T_T - T_R$) varies with temperature, as does also the correction of ρ necessary to force the equality, $T_T = T_R$.

c. Empirical Emissivity Correction

In principle, Eq. 24 yields ρ values suitable for use at various temperatures by estimating the effective emissivities resulting from the geometric arrangement. Empirical determinations are more conveniently made, however, by using a pilot test target. The pilot target is identical to all the other test targets, except that it has a thermocouple secured in a tiny well, drilled from the cylindrical surface into its interior like that of the reference target.

The temperature of the reference target is set at some desired value by adjusting the reference voltage potentiometer (shown in Fig. 26).

With ρ set at the zeroed value of 0.500, the test-target loop adjusts to produce a controlled temperature of the test target near to, but not necessarily equal to, that of the reference target; ρ is then adjusted to make the temperatures equal. Such potentiometer settings, ρT_1 , ρT_2 , ..., ρT_n for temperatures T_1 , T_2 , ..., T_n are then taken as applicable to use in the controlled heating of any other of the test targets in the series with equal emissivity.

Figure 28 shows a typical example of the variation of the potentiometer readings with temperature. Note from the plot that the ρ values are also somewhat dependent upon the sensitivity range of the radiometer; consequently, the radiometer sensitivity settings corresponding to each potentiometer reading must be recorded when the ρ values are taken in preparation for a series of molecular-beam exposures.

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Fig. 28. Potentiometer Setting, ρ , vs Temperature

d. Preliminary Steps of Operation

With the radiometer and other electronic components warmed up sufficiently to give steady performance, the first step in the use of the equipment is to check the zero balance of the positive and the negative detector-integrators labeled (-) DET. in Fig. 27, by injecting a common signal. The potentiometer is set at 0.500, and the error meter is nulled by adjusting a trimmer potentiometer that controls the relative gains of the detector-integrators. The common signal for this test is conveniently supplied by intercepting the radiometer's field of "view" by a black-painted electric hotplate placed between the radiometer and the nodding mirror. The operation of the nodding mirror preserves the normal performance of the system while the signal fed through the radiometer to the two detector-integrators remains constant.

Under bake-out conditions, when the equilibrium temperature in the vacuum chamber is about 150°C, the relative emissivities of the test target are checked as discussed in Section 2.a of this appendix. If these do not vary by more than the equivalent of $\pm 0.4^\circ$, the chamber is cooled to room temperature and the pilot test target described in Section 2.c of this appendix is used to determine the potentiometer readings necessary to force the test-target loop to produce desired temperatures in the test targets. These readings and the corresponding radiometer sensitivity data are then used to effect controlled heating of each test target as it is moved into position for a timed exposure of its back side to a molecular beam.

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