

Deposition of Atomic Beams*

SOL WEXLER

Argonne National Laboratory, Lemont, Illinois

A. INTRODUCTION

FROM the increasing number of investigators using condensation methods at present, it appears that the techniques of detecting molecular beams have gone through a complete cycle, and we are now back to the methods used in the early 1920's by Stern, Estermann, and their collaborators.¹ The reasons for the renewed interest in deposition of beams are quite clear: (1) Other methods of detection, such as by surface ionization and by pressure, are applicable to relatively few elements. An exception is possibly the so-called "universal detector" advanced by Wessel and Lew, Schutze and Bernhard, Ramsey, and others.² This procedure of ionization of an atomic beam followed by mass analysis, however, is confined to detection of major constituents of the beam. For studies on radioactive nuclides, stringent enrichment and purification procedures are required to fulfill this requirement. (2) Efforts of many workers in the field of molecular beams are directed towards the determination of nuclear spins and nuclear moments of radioactive atoms.³ Since sensitive methods of measuring the radioactivity of solid samples are available, it is only necessary to collect the beam of active atoms on a surface prior to the activity measurements. This procedure appears to have general applicability, for its use is limited only by the need of a sufficient concentration of active atoms in the beam to avoid excessively long deposition times.

If deposition technique is to be suitable for determination of intensities of atomic beams, an unchanging and preferably high fraction of the atoms in the beam must condense on the collecting surface on first collision. The efficiency of sticking is known to be dependent on a variety of factors, such as the composition and the density of the beam and the nature and temperature of the surface. This paper reviews the knowledge in this field for the benefit of workers in the field of molecular beams. A twofold objective was considered: assembling

in one place of information of use to "molecular beamists"; and establishment of some criteria for selection of a surface material with high efficiency of deposition from beams of atoms. Results considered of particular importance in this regard are those on condensation or sticking coefficients, "critical temperatures" for condensation, and binding energies of condensed atoms on surfaces.⁴ Two theories of deposition of atomic beams are also reviewed.

B. STICKING COEFFICIENTS

1. Experimental Results

With the exception of data presented in subsequent tables, extant results of determination of condensation or sticking coefficients are assembled in Table I. The coefficient is the fraction of the atoms striking a surface which remain fixed on the surface. Information is arranged in alphabetical order by chemical symbol of the elemental constituent of the beam or vapor. Under each impinging atom are the various surfaces employed in the measurements (Column 2) and the corresponding condensation coefficients observed (Column 3).

The information in the table has been drawn from a variety of experimental techniques, and no attempt is made to describe them in detail here. In several of the experiments a beam of the atoms under study was allowed to fall on various surfaces, different in composition or in method of preparation (for example, Yang,⁵ Devienne,⁶ Goodman and Wexler,⁷ and Hobson *et al.*⁸). In others the sticking factor was derived indirectly from the rate of evaporation of a hot filament (for example, Jones *et al.*,⁹ and Marshall *et al.*¹⁰) or the torque produced on the surface by reflection of atoms off it.¹¹ When comparisons can be made among the results of different investigators, reasonable agreement is found in the Cd and Hg studies despite differences in methods

* Work performed under the auspices of the U. S. Atomic Energy Commission.

¹ I. Estermann and O. Stern, *Z. physik. Chem.* **106**, 399 and 403 (1923); W. Gerlach and O. Stern, *Ann. Physik* **74**, 673 (1924); **76**, 163 (1925); O. Stern, *Z. Physik* **2**, 49 (1920).

² G. Wessel and Hin Lew, *Phys. Rev.* **92**, 641 (1953). F. Bernhard, *Z. angew. Phys.* **9**, 68 (1957); W. Schutze u. F. Bernhard, *Z. Physik* **145**, 44 (1956); N. F. Ramsey, (unpublished work). See also the technique of surface ionization by Davis, Nagle, and Zacharias, *Phys. Rev.* **76**, 1068 (1949).

³ See, for example, A. Lemonick and F. M. Pipkin, *Phys. Rev.* **95**, 1356 (1954); Hobson, Hubbs, Nierenberg, and Silsbee, *Phys. Rev.* **96**, 1450 (1954); D. A. Gilbert and V. W. Cohen, *Phys. Rev.* **97**, 243 (1955); L. S. Goodman and S. Wexler, *Phys. Rev.* **99**, 192 (1955); E. H. Bellamy and K. F. Smith, *Phil. Mag.* **44**, 33 (1953).

⁴ A review of condensation of molecules on surfaces in vacuum is given by F. M. Devienne, *Mém. sci. phys.* **53**, 1-86 (1952). R. G. J. Fraser, *Molecular Rays* (Cambridge University Press, London, 1931), and *Molecular Beams* (Methuen and Company Ltd., London, 1937) also contain detailed discussions of deposition of molecular beams.

⁵ Yang, Simnad, and Pound, *Acta Met.* **2**, 470 (1954).

⁶ F. M. Devienne, *Compt. rend.* **238**, 2397 (1954).

⁷ L. S. Goodman and S. Wexler, Argonne National Laboratory (unpublished data).

⁸ Hobson, Hubbs, Nierenberg, Silsbee, and Sunderland, *Phys. Rev.* **104**, 101 (1956) and unpublished data.

⁹ Jones, Langmuir, and Mackay, *Phys. Rev.* **30**, 201 (1927) as corrected by M. Volmer, *Kinetik der Phasenbildung* (T. Steinkopff, Dresden and Leipzig, 1939).

¹⁰ Marshall, Dornte, and Norton, *J. Am. Chem. Soc.* **59**, 1161 (1937).

¹¹ G. Wessel, *Z. Physik* **130**, 539 (1951).

and techniques. But this cannot be said for measurements on silver and iron. The spread in values even for a given combination of beam and surface suggests that reproducibility of surfaces is a major problem in these experiments.

Despite scarcity of available data and lack of precision, some general conclusions may be drawn:

(1) Alkali atoms stick well to oxide-free metallic surfaces at room temperature, but not to ordinary surfaces. Yet sodium beams stick strongly to glass¹² and potassium to quartz.¹³

(2) Elements of Group I-b (Au, Ag, and Cu) condense on first collision on almost any surface, whether it has been prepared freshly under high vacuum conditions or is the usual surface encrusted with oxide and/or gas. However, Group II-b atoms are radically different in this respect. When Cd, Zn, and Hg are the impinging particles, the surface must be freshly deposited under high vacuum to ensure high efficiency of sticking. Even then a freshly deposited Al substrate apparently forms an oxide coat very quickly and is therefore unsuitable for catching Zn atoms.

(3) If a surface is formed by evaporation in vacuum, it should be used immediately for depositing a beam, for the sticking coefficient at room temperature is found to decrease with the time between preparation and measurement.¹⁴ A fresh surface is observed to change in a few minutes even at a pressure of 10^{-8} mm.^{15,16} At 150°C the decrease of the sticking coefficient with time is not measurable, suggesting that a gas film on the surface is responsible for reflection of atoms impinging on it. At 150°C the film would be expected to be absent.

2. Effect of Surface Temperature on Sticking Coefficient

Most of the data in Table I were obtained with the surfaces at room temperature. For beams of Cd, Ag, Cu or Hg atoms striking various surfaces, Frauenfelder¹⁴ found that the sticking coefficient depends very little on temperature in the range from 20 to 200°C. Also Wessel¹¹ observed that the coefficient for Ag atoms on a silver surface exceeds 0.92 up to the melting point (1234°K). For potassium depositing on quartz, the constant remains unity from -180 to 20°C (Wegener¹³). Yet Devienne⁶ observed sharp decreases in the probability of sticking of Sb and Au beams when the surface temperature is raised above 25°C. Representative data are presented in Table II.

A marked increase in condensation efficiency is found when the surface temperature is far below 25°C. An

TABLE I. Condensation coefficients of metallic atoms.^a

Element in vapor or beam	Surface	Condensation coefficient	Reference
Ag	Ag (deposited in vacuum)	0.2-0.4	b, e, d
	Mechanically cleaned Ag, Cu, or Au	0.3-0.6	e
	Ag	>0.92	f
	Au (polished and etched) at 192°C	1.0	g
Glass at 192°C		0.2- >0.7	g
	Ag, Cu, or Au freshly deposited in vacuum	0.4-0.8	e
Au	Glass, Cu, Al	0.90-0.99	h
Be	Be	1.0	i, k
Cd	Glass or metal	very small	i, k
	Glass, mica, Al, silicone-covered glass	~0	l
	Al (freshly deposited in vacuum)	1.0	m
	Glass, mica, or metal	0.0001-0.01	e
Cu	Ag, Cu, Au, Sn (freshly deposited in vacuum)	0.3-0.6	e
	Cd	0.4-0.7	j
	Cd (very pure)	0.4-0.7	n
	Cd (very pure)	<1.0	n
	Cd (ordinary)	0.01-0.1	n
	Cd (polished)	1.0	f
	Cu (deposited in vacuum)	0.2-0.4	b
Cu (freshly deposited in vacuum)	0.4-0.6	e	
Cs	Cu (deposited in vacuum)	1.0	p
	Al, Ni	0	q
	Ta	0.5	q
Fe	W	0.7	q
	Cu at liquid N ₂ temperatures	1.0	r
	Fe (deposited in vacuum)	0.2-0.4	b
Hg	Fe	1.0	f
	Glass or metal	very small	i, k
	Glass, mica, or metal	<0.01	e
	Au (freshly deposited)	0.2-0.4	e
	Solid Hg	0.8-0.9	s, t
K	Freshly dropped Hg	1.0	u
	Hg at 55-64°C	0.7	u
Mo	Quartz	1.0	v
	K (single crystal)	≈1	w
Na	Mo (deposited in vacuum)	0.2-0.4	b
	Brass, Ni, Cu	very small } probably 0	x
Ni	Copper-amalgam	0.1-1.0	b
	Ni (deposited in vacuum)	0.2-0.4	
Pt	Pt	1.0	o
	Brant sulfur	1.0	y
	Brass	0.1	
	Ag	0.07	
Pt	0.24		
Sb	W	0.21	z
	Al	0.26	
	Cu	0.325	
W	Glass	0.311	h
	W (deposited in vacuum)	0.2-0.4	b
Zn	Zn	1.0	f
	Al (evaporated in vacuum)	0	m
	Ca, Cu,	1.5-1.6	
	Ag	0.9	

^a Indium beams have been collected with high efficiency on Cu disks at liquid N₂ temperature [L. S. Goodman and S. Wexler, *Phys. Rev.* **108**, 1524 (1957)], but no quantitative measurements of the sticking coefficient were made. Also Nierenberg *et al.* used a burnt sulfur surface at room temperature to deposit beams of gallium, thallium, cesium, and silver. [Nierenberg, Shugart, Silsbee, and Sunderland, *Phys. Rev.* **104**, 1380 (1956); Hubbs, Nierenberg, Shugart, and Worcester, *Phys. Rev.* **105**, 1928 (1957) and unpublished data.] Collection of As⁷⁶ beams on copper surfaces at -120°C has been achieved by Christensen, Bennewitz, Hamilton, Reynolds, and Stroke, *Phys. Rev.* **107**, 633 (1957). In addition, E. Lipworth and H. L. Garvin [*Bull. Am. Phys. Soc. Ser. II*, **2**, 316 (1957)] have deposited iodine on Ag-coated buttons, and Hubbs, Marrus, Nierenberg, and Worcester [*Bull. Am. Phys. Soc. Ser. II*, **2**, 316 (1957)] have collected Pu²³⁹ beams on platinum surfaces.

- ^b See reference 9.
^c P. Harteck, *Z. physik Chem.* **134**, 1 (1928).
^d J. Fischer, *Z. anorg. u. allgem. Chem.* **219**, 367 (1934).
^e See reference 14.
^f See reference 11.
^g See reference 5.
^h See reference 6.
ⁱ Holden, Speiser and Johnston, *J. Am. Chem. Soc.* **70**, 3897 (1948).
^j See reference 19.
^k See reference 20.
^l See reference 17.
^m P. Garen and P. Prugne, *J. Phys. Radium* **15**, 829 (1954).
ⁿ K. Bennewitz, *Ann. Physik* **59**, 193 (1919). See also A. C. Edgerton and F. V. Raleigh, *J. Chem. Soc.* **123**, 3024 (1923).
^o M. Volmer, *Kinetik der Phasenbildung* (T. Steinkopff, Dresden and Leipzig, 1939).
^p See reference 10.
^q See reference 42.
^r See reference 7.
^s M. Volmer and I. Estermann, *Z. Physik* **7**, 1 (1921).
^t M. Knudsen, *Ann. Physik* **47**, 697 (1914).
^u M. G. Rossman and J. Yarwood, *Brit. J. Appl. Phys.* **5**, 7 (1954).
^v See reference 13.
^w F. Hock and K. Neumann, *Z. physik Chem.* **2**, 241 (1954).
^x See reference 31.
^y See reference 8.
^z See reference 22.

¹² N. F. Ramsey, *Molecular Beams* (Clarendon Press, Oxford, 1956), p. 376.

¹³ H. Wegener, *Z. Physik* **140**, 465 (1955).

¹⁴ H. Frauenfelder, *Helv. Phys. Acta* **23**, 347 (1950).

¹⁵ J. S. Morrison and J. K. Roberts, *Proc. Roy. Soc. (London)* **A173**, 1 (1939).

¹⁶ E. W. Mueller, *Z. Physik* **126**, 642 (1949).

TABLE II. Effect of surface temperature on condensation coefficient of Sb and Au beams (Devienne).

Beam	Surface	Temperature of surface	Condensation coefficient
Sb	glass	25°C	0.311
	glass	125	0.053
	Cu	170	0.325
	Cu	265	0.201
Au	glass, Cu, Al	25	0.90-0.99
	Cu	350	0.84
	glass	360	0.50
	Al	320	0.715
	Al	345	0.37

example is that of Cs atoms depositing on copper surfaces⁷ (see Sec. C).

3. Variation of Sticking Coefficient with Thickness of Deposited Layer

In an extensive study of the factors affecting the magnitude of sticking coefficients, Devienne¹⁷ measured their dependence on the thickness of the deposited layer. For every combination of impinging atoms and surface, the value increased sharply with the thickness of built-up deposit. Typical data appear in Table III.

From these and similar measurements Devienne concluded that the nature of the surface is fairly important if the condensed layer is less than 20 Å thick, but is relatively unimportant for deeper layers. Thus condensation of Sb and Cd is influenced by layers already deposited. This behavior is expected since the deposition of thick layers is an application of the technique of preparing freshly evaporated surfaces to enhance the sticking probability. The chance that the condensation coefficient may increase during deposition of the beam in a magnetic resonance experiment is, however, slight. Calculations based on usual beam densities and times of deposition indicate that far less than a monolayer is condensed in a typical experiment if the condensed material is assumed to be uniformly spread over the surface.

TABLE III. Change of condensation coefficient with thickness of deposited layer (Devienne).

Beam	Surface	Thickness (Å)	Condensation coefficient
Sb	Cu	1.9	0.401
		2.2	0.417
		4.9	0.456
		39.6	0.608
		437.8	0.772
Cd	Cu	0.8	0.037
		4.9	0.257
		6	0.240
		42.4	0.602

¹⁷ F. M. Devienne, J. phys. radium **14**, 257 (1953).

4. Effect of Dissimilarities in the Crystal Lattices of Elements in Beam and Target

Yang, Simnad, and Pound⁵ have reported a significant variation of the condensation coefficient of silver beams with the disregistry between the lattice constant of Ag and that of the condensing substrate. The lattice misfit is defined by the relation

$$D = \frac{\alpha_{\text{Ag}} - \alpha_{\text{target}}}{\alpha_{\text{Ag}}} \times 100\%, \quad (1)$$

where α is the dimension of the unit cell. Results of their measurements are shown in Table IV. The temperature of the target was 192°C in order to prevent formation of a film of gas on the surface. The time of condensation was one hour, during which time less than one monolayer of silver was deposited. There is clear indication here that the potency of the substrate for condensing atoms on first collision varies inversely with the disregistry between the lattice constant of the crystal of the beam substance and that of the substrate.

TABLE IV. Effect of lattice misfit on condensation coefficient.

Target	Condensation coefficient	Lattice misfit (%)
Ag	1.0	0
Au	0.99	0.18
Pt	0.86	3.96
Ni	0.64	13.7
glass	0.31	

C. CRITICAL TEMPERATURES AND SUPERSATURATIONS

The first investigators observed that, though condensation did not occur at room temperature, in many cases a sufficient decrease in target temperature caused efficient deposition of a beam of atoms. For a particular beam and surface material there appeared to be a temperature above which no permanent deposit was formed. There was also a critical minimum transitional beam intensity below which no permanent deposit was formed no matter how long the surface was exposed to the beam.¹⁸ Knudsen¹⁹ and Wood²⁰ found that Cd and Hg condense on glass and metals below a certain "critical temperature" but are desorbed again above that temperature. They assumed that the condensation coefficient increased abruptly from zero to unity as the surface temperature was lowered through the transition point. However, Gen *et al.*²¹ report film formation above the critical temperature after long periods of observation. The earlier assumption is also disputed by

¹⁸ R. G. Fraser, *Molecular Rays* (Cambridge University Press, London, 1931).

¹⁹ M. Knudsen, Ann. Physik **50**, 472 (1916).

²⁰ R. W. Wood, Phil. Mag. **32**, 364 (1916).

²¹ Gen, Lebedinsky, and Leipunski, Physik Z. Sowjetunion **1**, 571 (1932).

Devienne.²² Indeed, on the basis of measurements on beams of Cd and Hg, Frauenfelder¹⁴ denies the existence of any critical temperature of condensation for pure metallic surfaces which are free of oxide coat.

Contrary to what one might at first expect, the critical condensation temperature is not the temperature of the surface at which the vapor pressure of the beam material is too low for the deposit to evaporate. Once the first trace is formed the deposit will grow if the effective beam pressure is greater than the vapor pressure, but for deposition of the first nuclei the target temperature must be considerably lower.²³ The actual temperature depends on the materials in the beam and target, on the intensity of the beam, and on its geometry, principally its width.^{24,25} By varying the beam intensity and/or the surface temperature one can get anything from complete condensation to none at all. For example

copper. His results could be fitted to a relation of the form

$$\nu_c = 4.7 \times 10^{22} e^{-2840/T} \text{ atoms/sec cm}^2, \quad (2)$$

in which a strong effect of the absolute temperature is indicated. For example, ν_c decreases from 2×10^{16} atoms $\text{sec}^{-1} \text{cm}^{-2}$ at -80°C to 4×10^{12} at -155°C . The relation between critical density and temperature was first derived by Frenkel²⁷ (see Sec. E). Cockcroft measured the critical density for deposition of Cd beams on copper for surface temperatures ranging from -92° to -155°C , and for Cd on silver, copper, and glass at -137°C . Since no differences in critical density were found in the latter studies, it was suggested that gas films caused all the surfaces to act like. Cd deposited more readily on a freshly deposited Ag surface than on an old one, and if the surface was baked at 350°C to remove the gas film prior to deposition, the critical density decreased by a factor of ten. He concluded that if surface films could be eliminated, the phenomenon of critical density would not exist for many surfaces.

Rhodin²⁸ has determined critical pressures for condensation of Al on glass and on single crystals of several minerals.

Yang *et al.*²⁹ have studied the problem of critical density in great detail. However, they consider the critical supersaturation to be of greater significance in the understanding of deposition and nucleation phenomena. The critical supersaturation is defined as the ratio of the equivalent pressure of the beam to the vapor pressure of the beam substance at the target temperature at which deposition first becomes observable. The equivalent pressure of the beam is that equilibrium pressure of vapor for which the number of atoms per second striking a unit area of target is the same as for the actual beam. The relation derived by them for the critical supersaturation S_c for condensation on a target at a temperature T is

$$S_c = (\rho_0/\rho) (f_0/\pi r^2) (T/T_0)^{1/2}, \quad (3)$$

in which ρ is the vapor pressure of the beam material at the target temperature, T_0 the temperature of the oven producing the beam, ρ_0 the vapor pressure of the beam material in the oven, f_0 the area of the oven orifice, and r the distance between oven and target.

Critical supersaturations of the order of 10^{13} were found for silver depositing on a glass surface at 192°C . An analysis of Cockcroft's data²⁶ for Cd condensing on copper at temperatures from 118 to 181°K yields critical supersaturations ranging from 10^{33} to 10^{19} , respectively. On the other hand, Devienne³⁰ finds adsorption of Cd beams on surfaces at 300°K at much lower supersaturations than those taken from extrapolation of Cockcroft's results.

TABLE V. Critical temperatures for condensation.

Beam material	Surface	Critical temperature ($^\circ\text{C}$)	Reference
Ag	glass	over 575°	a-c
Cd	Ag	-86° to -66°	d
	Cu	-111° to -74°	d
	glass	-140° to -75°	a
	glass	-110° to -50°	d
	glass (chemically cleaned)	-80°	e
	glass (cleaned, baked at 450°C)	$>290^\circ$	e
	glass	...	f
Cu	mica	-77° to -80°	g
	paraffin	-67° to -70°	g
Hg	glass	350° to 575°	a, e
	glass (chemically cleaned)	-140° to -130°	a, e
	glass (cleaned, baked at 450°C)	20°	e
Sn	Ag	-120° to -88°	d
	glass	...	f
Zn, Cd, Mg	glass	-183° to -78°	a

^a See reference 19.

^b W. Gerlach and O. Stern, Ann. Physik **74**, 673 (1924).

^c O. Stern, Z. Physik **2**, 49 (1920).

^d See reference 24.

^e M. Seddig and G. Haase, Kolloid-Z. **114**, 169 (1949).

^f Olsen, Crittenden, Jr., and Hoffman, Phys. Rev. **76**, 1891 (A) (1949).

^g J. Chariton and N. Semenov, Z. Physik **25**, 287 (1924).

one can obtain condensation of the umbra but not the penumbra of an atomic beam. This results from the target temperature being low enough to allow deposition of a beam of high intensity but not one of low intensity.

Results on critical temperatures gathered from the literature appear in Table V. One notes that "critical temperatures" far below room temperature were observed by early workers for beams of Cd and Hg. Yet Frauenfelder¹⁴ could find no transition temperature for beams of Zn, Cd, and Hg condensing on clean metallic surfaces even when the temperature was raised to 250°C .

In 1928 Cockcroft²⁶ measured the dependence of the critical density ν_c of Cd beams on the absolute temperature T of a condensing surface of mechanically polished

²² F. M. Devienne, Mém. sci. phys. **53**, 1 (1952).

²³ I. Estermann, Revs. Modern Phys. **18**, 300 (1946).

²⁴ I. Estermann, Z. Electrochem. **31**, 441 (1925); Z. Physik **33**, 320 (1925).

²⁵ J. Chariton and N. Semenov, Z. Physik **25**, 287 (1924).

²⁶ J. Cockcroft, Proc. Roy. Soc. (London) **A119**, 295 (1928).

²⁷ J. Frenkel, Z. Physik **26**, 1117 (1924).

²⁸ T. N. Rhodin, Discussions Faraday Soc. **5**, 215 (1949).

²⁹ Yang, Birchenall, Pound, and Simnad, Acta Met. **2**, 462 (1954).

³⁰ F. M. Devienne, J. phys. radium **13**, 53 (1952).

These values may be compared with the supersaturation of a sodium beam obtained in a typical atomic beam experiment. If we take 1 mm as the vapor pressure of Na in the oven ($T_0=714^\circ\text{K}$), 298°K as the temperature of the condensing surface, an oven slit area of 0.032 cm^2 (i.e., a slit $0.010\text{ in.}\times 0.50\text{ in.}$), and 100 cm as the distance between oven and collecting surface, since the vapor pressure of Na at room temperature is about $1.8\times 10^{-10}\text{ mm}$, S becomes 3.6×10^3 . Since this is so far below usual critical supersaturation values, it explains why sodium beams stick so poorly to most ordinary surfaces.³¹

An attempt was made by Yang *et al.*²⁹ to find a relation between the critical supersaturation of a Na beam for deposition and the lattice registry between crystalline Na and the condensing substrate. Similar supersaturations (10^{13} to 10^{19}) were found for the four metal surfaces (Ag, Pt, Cu, and Ni) used in the temperature region of 210° to 159°K . It was suggested that the surfaces of all the metals were probably masked by adsorbed layers of residual gas despite degassing and deoxidizing with H_2 just before use.

D. SURFACE BINDING ENERGIES

Casual considerations suggest that the binding energy by which a condensed atom is held to a surface (i.e., the energy required to transfer the atom from its lowest energy state on the surface to the free state) is a key to the extent of deposition on first collision. A combination of projectile and surface for which the release of energy on condensation is large (greater than 1 eV) would be expected to be more conducive to the atoms remaining on the surface than a combination for which the binding energy is low. In the former case, exchange or overlap forces act on the deposited atom and a relatively strong metallic bond is formed between atom and substrate. However, if the energy of binding is only of the order of tenths of an electron volt, only the relatively weak van der Waals forces hold the condensed atom to the surface, and the atom is more apt to be re-evaporated. The relation between desorption probability W and binding energy E is of the form³²

$$W = \text{const}e^{-E/kT}, \quad (4)$$

which indicates a marked dependence. Frauenfelder¹⁴ uses this relation to measure the binding energy of Cd atoms on a silver surface.

In the absence of data on sticking coefficients, information on binding energies may therefore be of use in selecting a satisfactory condensing surface. The available material is presented in Table VI. Attention is called to the much higher binding energy for Cd atoms on freshly deposited Ag as compared with that

for silver cleaned mechanically. Apparently gas and oxide films on the surface in the latter case hinder formation of a metallic bond. Marked decreases of binding energy are also observed when substrates prepared in vacuum are allowed to stand before condensation of the material under study.¹⁴ This behavior is blamed on the strong influence of adsorbed gases on surface forces.

Strong adherence of alkali atoms to a tungsten surface is indicated by the high energy released on deposition. Since tungsten usually is coated with oxide, the strong attachment of alkali atoms may be caused by adsorption in an ionic state with the formation of an electric double layer at the surface.³³

E. DISCUSSION

No better illustration of the great lapse in time between the early studies in condensation phenomena involving atomic beams and more recent renewed interest can be found than in the theoretical treatments

TABLE VI. Binding energies of metallic atoms.

Metal	Surface	Binding energy (ev)	Reference
Al	mica	0.8-0.95	a
	NaCl	0.5-0.7	a
Cd	Cu, glass	0.13-0.15	b, c
	Ag	0.22	b
	Ag, glass	0.22-0.25	c
	freshly deposited Ag	1.5-1.7	d
Cs	W	3.6	e
Hg	Ag	0.11	b
K	W	2.9	e

^a See reference 28.

^b See reference 24.

^c See reference 26, p. 295.

^d See reference 14.

^e F. Knauer, Z. Physik 125, 278 (1949).

of the subject. The behavior of beams of atoms impinging on surfaces has been considered theoretically in papers separated in time by as much as thirty years. We consider the principal early paper³⁴ and one of the main recent studies. Frenkel²¹ began with the proposal of Langmuir³⁵ that an atom which strikes a surface is not immediately reflected but stays on the surface for a finite time. The mean time τ of adsorption, or "dwelling time" of an atom, is shown by statistical methods to be given by

$$\tau = \tau_0 e^{+\mu_0/kT}, \quad (5)$$

where τ_0 is the period with which an adsorbed atom oscillates perpendicular to the surface and μ_0 is the

³³ Higuchi, Ree, and Eyring, J. Am. Chem. Soc. 77, 4969 (1955).

³⁴ Theoretical discussions in the 1920's, other than the one outlined here, were by I. Estermann and O. Stern, Z. physik. chem. 106, 399, 403 (1923), J. D. Cockcroft, Proc. Roy. Soc. (London) 119, 293, 306 (1928), M. Volmer, Z. physik. Chem. 115, 253 (1925), and I. Estermann, Z. Electrochem. 31, 441 (1928).

³⁵ I. Langmuir, Phys. Rev. 8, 149 (1916).

³¹ J. A. Dalman and S. Wexler, Argonne National Laboratory (unpublished data).

³² S. Brunauer, *The Adsorption of Gases and Vapors* (Princeton University Press, Princeton, 1943), Vol. 1, p. 61.

heat of vaporization. During their stay on the substrate individual atoms move about at random, much like a two-dimensional gas. Collisions between atoms result in formation of atomic pairs with much longer lifetimes than those of single atoms. These atomic pairs in turn act as centers of condensation for other atoms. Assuming only mono- and diatomic molecules on the surface and considering the rates of arrival and of departure of atoms from the surface, Frenkel showed with statistical methods that the critical density γ_{crit} of a beam of atoms for deposition was

$$\gamma_{\text{crit}} = (4\sigma_0\tau_0)^{-1}e^{-\mu/kT}, \quad (6)$$

where σ_0 is the cross section of the atom given by gas kinetic theory, τ_0 the period of oscillation of an adsorbed atom perpendicular to the surface, and μ is the sum of the energy of adsorption of a single atom to the substrate and the dissociation energy of a pair of atoms. The similarity of this relation to the one found experimentally by Cockcroft [Eq. (2)] is obvious. Thus for a Cd beam $(4\sigma_0\tau_0)^{-1}$ is equal to 4.7×10^{22} and $\mu/k = 2840$, so that if the cross section is 2×10^{-16} cm², the period of oscillation becomes 2.6×10^{-9} sec. The mean life of an atomic pair on a surface at -100°C then is $2.6 \times 10^{-9}e^{2840/173} = 3.4 \times 10^{-2}$ sec, using a relation analogous to Eq. (5) for the case of a doublet. Similar equations are derived for cases in which condensation nuclei comprising more than two atoms are assumed to form. Only the constants are found to change.

In more recent work on this problem,³⁶ Pound, Sinnad, and Yang³⁷ begin with the same model as Frenkel. Every atom from an atomic beam which strikes a surface is assumed to be temporarily adsorbed and to come to thermal equilibrium with the substrate. These atoms move at random over the surface until they join a growing cluster of atoms (called an embryo) or stable nucleus of atoms, or leave the surface by evaporation. A rate equation for nucleation of metal crystals on substrates is derived on this basis, using statistical methods similar to those employed in the treatment of nucleation in phase transformations.³⁸

During the dwelling time of an atom which has struck a surface from an atomic beam it may join with another such atom, and this diatomic species with another atom. In this manner a growing unstable embryo is formed. These embryos are assumed to form uniformly over the the substrate surface rather than only at preferred sites for nucleation, such as dislocations, cracks, and impurities. After the embryo has grown to a certain critical size, it has an even chance of growing into a stable nucleus for nucleation. Aggregates smaller than this critical size will in general tend to evaporate. For

water vapor condensing on droplets,³⁹ the number of molecules in a critical nucleus is about 100.

At equilibrium the concentration of critical nuclei (number per cm² of surface), each containing i^* adsorbed atoms, is shown³⁷ to be

$$n(i^*) = n(1)e^{-\Delta F^*/kT} \quad (7)$$

where $n(1)$ is the equilibrium concentration of adsorbed single atoms and ΔF^* is the standard free energy of formation of critical nuclei. Since the rate at which nucleation (and accordingly deposition) proceeds is equal to the concentration of critical nuclei multiplied by the rate at which single adsorbed atoms join the critical nuclei, one may write

$$I = \alpha n(i^*), \quad (8)$$

where α equals the circumference of the intersection of a nucleus with the substrate surface multiplied by the frequency with which the randomly moving atoms strike the nucleus. From such varied sources as the kinetic theory of gases, thermodynamic and statistical concepts, and random-walk considerations, expressions are derived for $n(1)$, ΔF^* , and α . The final result shows the deposition rate of an atomic beam to depend on many factors:

$$I = [\gamma(\sin\theta)a_0/2mk\nu][(\phi')^2/-\Delta F_v T] \times \exp[(-2\Delta F_{ad}^0 + \Delta F_D + \Delta F^*)/kT], \quad (9)$$

where γ = free energy per unit area of the interface between nucleus and vapor, θ = contact angle between surface of condensation nucleus and plane of substrate, a_0 = lattice parameter of the nucleus, m = mass of the adsorbed atom, k = Boltzmann constant, ν = vibration frequency of the surface atoms of the substrate and the nucleus (assumed to be the same), ϕ' = the equivalent partial pressure of the vapor of the condensed material which gives the same collision rate as the atoms in the beam, ΔF_v = free energy per unit volume for the transformation of vapor to condensed solid, ΔF_D = free energy of activation for surface diffusion, ΔF_{ad}^0 = standard free energy of adsorption, ΔF^* = standard free energy of formation of the critical nuclei, and T = absolute temperature of the substrate.

A rate equation similar in form has been derived by Hollomon and Turnbull^{40,41} assuming direct addition of atoms from the vapor to critical nuclei without intermediate surface diffusion. In a typical example the surface diffusion model leads to a nucleation rate 10^2 – 10^3 times as high as that given by the mechanism of direct addition.

No experimental test of Eq. (9) has taken place as yet. However, a relation derived from it, describing the

³⁶ See also M. Volmer, *Kinetik der Phasenbildung* (T. Steinkopff, Dresden and Leipzig, 1939) for a detailed discussion of deposition of beams.

³⁷ Pound, Sinnad, and Yang, *J. Chem. Phys.* **22**, 1215 (1954).

³⁸ R. Smoluchowski, "Nucleation theory" in *Phase Transformation in Solids* (John Wiley and Sons, Inc., New York, 1951), p. 149.

³⁹ M. Volmer and H. Flood, *Z. physik Chem.* **A170**, 273 (1934).

⁴⁰ J. H. Hollomon and D. Turnbull, *Progr. in Metal Phys.* **4**, 333–388 (1953).

⁴¹ J. H. Hollomon, "Heterogeneous nucleation" in *Thermodynamics in Physical Metallurgy* (American Society for Metals, Cleveland, 1950), pp. 161–177.

temperature dependence of critical supersaturation of atomic beams (Sec. C), shows good agreement with experiment. We consider the modification of relation (9) first. From thermodynamic concepts the standard free energy of formation ΔF^* of a critical nucleus is related to the bulk free energy change ΔF_v per unit volume in the transformation by

$$\Delta F^* = 16\pi\gamma^3 f(\theta)/3\Delta F_v, \quad (10)$$

where γ is the free energy per unit area of the crystal—vapor interface and $f(\theta)$ is a function of the contact angle θ between the nucleus and the substrate. ΔF_v in turn may be equated to the supersaturation p'/p by

$$\Delta F_v = -(RT/V) \ln p'/p, \quad (11)$$

in which p' is the equivalent vapor pressure which produces the same collision frequency on the surface as the atomic beam, p is the equilibrium vapor pressure of the condensed bulk metal at the temperature T of the substrate, and V is the molar volume. The critical supersaturation is taken to be the ratio of p'/p which makes $I=1 \text{ cm}^{-2} \text{ sec}^{-1}$. Then on inserting reasonable values for the factors in the coefficient of Eq. (9) and ΔF^* from Eq. (10), and ignoring ΔF_D since it is small relative to ΔF_{ad}^0 , relation (9) is altered to give the temperature dependence of the bulk free energy change per unit volume:

$$\left[\frac{1}{(\Delta F_v)_{\text{crit}}} \right]^2 = 3kT_{\text{crit}}(9 + \ln p'_{\text{crit}})/8\pi\gamma^3 f(\theta) - 3\Delta F_{ad}^0/8\pi\gamma^3 f(\theta), \quad (12)$$

under conditions of critical supersaturation. A plot of $[1/(\Delta F_v)_{\text{crit}}]^2$ against $T_{\text{crit}}(9 + \ln p'_{\text{crit}})$ is thus predicted to be a straight line. The data from measurements of critical supersaturations of Na beams on CsCl, Ag, Pt, Cu, and Ni do fall on straight lines in such a plot.³⁷ The results of the studies on the metal substrates all fall on the same line. Distinction between the surface diffusion and direct addition mechanisms cannot be made by this approach since the latter model also predicts a straight line when $[1/(\Delta F_v)_{\text{crit}}]^2$ is plotted against $T(9 + \ln p'_{\text{crit}})$. But the dependence of critical density on the width of the beam^{24,25} suggests the importance of surface diffusion in the mechanism of nucleation.

Nevertheless, the model is helpful in deciding whether nucleation takes place randomly over the substrate surface or only at a few active centers (e.g., at cracks and impurities). The discussion thus far has assumed a uniform substrate surface. But if only preferred sites induced nucleation, the coefficient of Eq. (9) and the free energy ΔF^* of activation would be lower. If the area covered by the preferred sites is only $\sim 10^{-8}$ of the surface, the coefficient of Eq. (9) is reduced sufficiently to change the factor $(9 + \ln p'_{\text{crit}})$ in Eq. (12) to $\ln p'_{\text{crit}}$. But the available data cannot be fitted to a straight line

plot of $(1/\Delta F_v)^2$ vs $T \ln p'_{\text{crit}}$. Thus this argument leads to the conclusion that nucleation is random over a large fraction of substrate surface, and not caused by relatively few active centers. Yet the studies on potassium vapor condensing on quartz indicate that nuclei are formed only at certain preferred sites.⁴² The fact that all the data on Na beams impinging on metal surfaces fall on the same straight line indicates that surface forces are shielded by films of adsorbed gas. Surface films are to be expected under the vacuum conditions employed in these experiments.^{15,16}

The rate equation [Eq. (9)] shows what experimental variables to adjust to encourage a high rate of nucleation (and accordingly a high efficiency of deposition) of an atomic beam on a collecting surface. The beam density (proportional to p') should be as high as is allowed by scattering in the gas, and the temperature of the collecting surface as low as possible, in agreement with the experimental results in Sec. C. Study of the data on "critical temperatures" for condensation (Table V) indicates that a surface held at liquid nitrogen temperatures would be highly efficient for condensing any atom on first collision. In an investigation⁷ which uses this technique in measurement of nuclear properties, virtually every Cs¹³⁴ atom was found to stick to a cold copper surface on first collision. No special care in preparing the copper was necessary. The data also reveal extremely high values of the critical temperatures for Ag and Cu beams on glass. This characteristic has been exploited by the Princeton group (Lemonick and Pipkin³) to deposit Cu⁶⁴ and Ag¹¹¹ on ordinary copper surfaces at room temperature.

Because of its position in the exponential term of Eq. (9), the standard free energy of adsorption exerts a pronounced effect on the rate of nucleation. Because of its direct relation to the free energy, a large binding energy of an atom to a surface would therefore be expected to enhance its deposition rate; and this is observed. A high coefficient of condensation is measured for a cesium beam on tungsten⁴³; the binding energy for this pair is high (Table VI), suggesting a strong metallic bond between projectile and surface in this case.

The literature on condensation coefficients demonstrates the high efficiency of deposition on chemically reactive surfaces. If the substrate is prepared under vacuum conditions so as to be free of oxide, water, oil, and possibly some adsorbed gases, which coat almost all surfaces, a large fraction of the impinging beam may be expected to remain on first collision, because the strong metallic bond with high energy, which can then exist between condensing particle and surface, would hinder re-evaporation. In an alternative method, an amalgam may be prepared in air and later the protective mercury coat driven off in vacuum, leaving a fresh surface free of the usual contaminants; or the surface

⁴² Reference 13, p. 473.

⁴³ V. W. Cohen and D. A. Gilbert, Brookhaven National Laboratory (unpublished data).

may be made active by hydrogen reduction. Some surfaces such as that of sulfur (and possibly also phosphorus) have been activated by burning for a very short period. The activation is attributed to a protective covering of sulfurous acid formed during the burning.⁸ In vacuum the H₂SO₃ evaporates, leaving a clean surface of sulfur.

Finally, attention should be drawn to the technique of driving ionized atoms into a surface by means of

electric fields. Smith and Bellamy³ ionized beams of Na²⁴ and K⁴² by surface ionization and then collected the ions, with apparently high yields, on disks maintained at a potential of 100 v negative with respect to the hot filament. Hobson *et al.*⁸ also performed experiments on alkali atoms with this technique. The efficiency of collection was found to be unity (for all collecting surfaces studied) if the potential difference between filament and disk exceeds three kilovolts.

Recent Determinations of Atomic Mass Ratios by Microwave Spectroscopy*

B. ROSENBLUM,[†] AND C. H. TOWNES, *Columbia University, New York, New York*

AND

S. GESCHWIND, *Bell Telephone Laboratories, Inc., Murray Hill, New Jersey*

INTRODUCTION

THE principal advances in determination of nuclear masses by microwave spectroscopy during the past several years have come from examination of diatomic molecules and, in particular, of some of the small corrections needed to convert experimentally determined frequencies of rotational spectra into values of mass ratios. New results from the microwave spectra of a number of diatomic molecules have become available since an earlier summary of mass information.¹ Furthermore, a rather precise and critical examination of various small corrections to mass measurements has been made in the molecule CO. From this the validity of the molecular theory involved has been confirmed to very high accuracy, and quite precise values of mass ratios of the C and O isotopes have been obtained.

To a first approximation, the atoms in molecules may be considered as point masses rigidly connected. In the particular case of diatomic molecules, precise measurement of the rotational frequencies, ν_1 and ν_0 , of two isotopic species can then give information about mass

ratios, since they are inversely proportional to the reduced masses of the two isotopic molecules, or

$$\frac{m_1}{m_0} = \frac{(\nu_0/\nu_1)(M/m_0)}{1 + (M/m_0) - (\nu_0/\nu_1)}, \quad (1)$$

where m_1 and m_0 are the masses of two isotopes of one of the atoms, and M is the mass of the second atom, which is assumed unchanged in the two cases. Expression (1) is sufficient to illustrate the determination of mass ratios from rotational frequencies. However, any precise work must use a more complete theory which allows for lack of rigidity of the molecule and the actual distribution of molecular electrons. This includes such effects as rotation-vibration interaction, centrifugal distortion, and anharmonicity of the potential function, all of which have been discussed in some detail in a number of places.^{1,2} In addition, two important corrections for the behavior of molecular electrons have recently been carefully examined.³ These two corrections will be briefly discussed and then followed by a review of the new results on mass ratios which are listed in Table I.

It has been realized for some time that lack of information about the contribution of molecular electrons, particularly those in the valence shell, to the kinetic energy of molecular rotation can easily limit the

* This paper was prepared at the suggestion of the Subcommittee on Nuclear Constants of the Committee on Nuclear Science of the National Research Council. This subcommittee consists of Ward Whaling, chairman, and F. A. Selove, G. A. Bartholomew, H. E. Duckworth, I. Perlman, W. H. Sullivan, and D. M. Van Patter, together with L. Lidofsky as consultant. Work partially supported jointly by the Signal Corps, the Office of Naval Research, and the Air Force Office of Scientific Research. Reprints may be obtained from the Publications Office, National Research Council, 2101 Constitution Avenue, Washington 25, D. C.

[†] Now at the University of California, Berkeley.

¹ Geschwind, Gunthur-Mohr, and Townes, *Revs. Modern Phys.* **26**, 444 (1954).

² C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).

³ Rosenblum, Nethercot, and Townes, *Phys. Rev.* **109**, 400 (1958).