

was observed. From 15 to 18 such experiments were carried out for each single crystal orientation in oxygen and argon.

A Cahn RG recording balance was used to detect the presence or absence of adhesion after contact and separation. The balance was housed in a totally enclosed system capable of evacuation and backfilling with the desired atmosphere. A silica specimen was suspended from the balance by means of a silica rod hang-down, and hung in the center of a silica furnace tube joined to the balance housing by means of a ground joint. The single crystal was supported from below and positioned just beneath the silica specimen. A vacuum linear motion feedthrough allowed the single crystal to be raised and lowered, allowing contact with and separation from the silica specimen. A thermocouple was positioned very near the single crystal to allow temperature determinations to be made. Prior to an experiment, the balance housing and furnace tube were evacuated and backfilled with either high-purity argon or oxygen (Matheson Co.) to one atmosphere pressure.

Since the Cahn balance is a null-positioning device, allowance had to be made for the balance arm to return to the null position for every weight change. Since minor vertical movement of the silica occurs during contact and separation, a small fused silica helix was inserted in the silica hangdown near the balance arm. This allowed the balance arm to retain its null position, while still indicating the forces being applied to it. The contacting force applied to the silica-metal interface was that corresponding to 100 mg, and an adhesion event was counted if the separating force was greater than that corresponding to 15 mg. The lower limit of 15 mg was chosen because factors such as electrical noise and building vibration obscured information below this level.

The temperature chosen for all the adhesion determinations was 590°C, since preliminary work on polycrystalline specimens indicated appreciable adhesion in this temperature region.

The probability that the same point on either the silica or gold single crystal was contacted more than once in a 200-contact sequence is considered to be very small, due to the exceedingly small area developed per contact, and minor lateral motion of the silica relative to the single crystal due to prior contacts.

The vitreous silica specimens were 2-mm rods (General Electric Type 201) with one end flame fused to a hemispherical shape. These specimens were heated overnight in oxygen at 1000°C, and were inspected microscopically for evidence of devitrification. If none was observed, they were then stored in a dessicator until used.

The gold specimens were single crystals (Materials Research Corp., 99.999% nominal purity) having the (100), (110), and (111) faces exposed. These orientations were cut from the same single crystal grown by the Bridgman method. The exposed surfaces were within two degrees of the desired orientation. Before each adherence determination, the gold single crystals were cleaned by immersion for 15 sec in *aqua regia* at 50°–60°C. The crystals were then thoroughly washed in distilled water, dried, and stored in a dessicator until used.

At the completion of the adherence determinations, indentation hardness measurements were made at room temperature for each orientation, using a Knoop indenter and a 25-g load.

The results of the adhesion determinations and microhardness measurements were plotted in Fig. 1. The dotted lines above and below each mean value indicate the 95% confidence intervals. The shaded portions are the results of the microhardness measurements. At the 5% level (*t* test), a significant difference is observed only for (100) in oxygen and argon, even though the mean values for (110) and (111) have slightly increased. The microhardness results are plotted as the reciprocal of the Knoop hardness to give a relative "softness" of each orientation. Comparing these softness results with the adhesion tendencies of the three orientations in argon, one can observe a rough correlation. It is concluded that the difference in adhesion tendencies of these orientations in argon can roughly be accounted for by the relative surface areas generated during contact, the softest plane allowing

a greater contact area to be developed, and a higher adhesion tendency to be observed for a constant contact load.

After each adhesion determination, the gold and silica surfaces were microscopically examined. The main features to be observed were on the silica surface. A cluster of surface disruptions of very small dimensions were observed on the part of the silica that was contacted. It is clear that when adhesive failure occurred, the silica surface was not left intact. In many instances, gold could be seen at many points on the silica surface due to adhesion. These observations reinforce the generally accepted conclusion that true adhesion failure is very rare—failure at an interface usually occurs by means of cohesive failure in either or both of the contacting materials.

Since specific chemical compound formation leading to adhesion is unknown between gold and silica, adhesion in argon can be ascribed to completely general London dispersion forces operating across the area generated during contact. These weak physical forces can lead to quite high forces needed for separation.¹³ Since these forces are nonspecific, they cannot explain the specific effect of oxygen on adhesion to the (100) plane of gold. It might be expected that oxygen could enhance diffusion of gold into silica across the interface by formation of positive gold ions and negative oxygen ions as diffusing entities. It would not be expected that this would lead to specific adhesion enhancement only for the (100) plane, however.

It has been observed in LEED studies that specific effects occur on gold surface orientations as a function of temperature.^{11,12} These effects have been interpreted in terms of the effect of unknown impurities derived from the bulk. The impurities have not been directly detected, and the observed surface structure are invariant with respect to the presence of oxygen.¹¹ For the purposes of this discussion, it will be assumed that even though the impurity does not apparently interact with oxygen *per se*, its influence is observed in the presence of oxygen and silica. The effect of these inferred impurities is to cause a transformation from a smooth plane to a roughened plane consisting of vacancies and adatoms. This roughening of the surface impurity layer occurs at lower temperatures for (110) and (111) than for (100). The interpretation is that at 590°C, this roughening has occurred for (110) and (111), but not for (100). These impurity atoms, even though they can still strongly interact with silica, are less tightly bound to gold and hence, will not strongly affect adhesion. For (100) where this has not yet happened, the impurities are still strongly bound to gold and enhance adhesion.

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Free Molecule Flow in an Annulus

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In a previous note,¹ the author has given results for the free molecule flow through several geometrically simple systems. The

results are upper bounds to the free molecule flow obtained with the aid of a variational method discussed by DeMarcus.^{2,3} The annulus with a finite length to spacing ratio is an additional simple geometry which is of practical interest in high vacuum work (cold traps). The free molecule flow through a long annulus has been given by Clausius.⁴ For a limited range of length to spacing ratio and radius ratio Davis⁵ has calculated the flow using a Monte Carlo technique.

This note will present the results of the upper bounds obtained for various annuli by the variational technique of DeMarcus.^{2,3}

Consider an annulus of length l , inner radius r_i , and outer radius r_o . Let L be the length to spacing ratio $[l/(r_o - r_i)]$ and σ be the radius ratio (r_i/r_o) . The transmission probability of the annulus is designated by Q , a dimensionless quantity from which the free molecule flow can be obtained by

$$G = \frac{1}{4} Q A \bar{v} \Delta p.$$

G is the free molecule flow in pressure volume units per unit time, A is the cross-sectional area open to flow $[\pi(r_o^2 - r_i^2)]$, $\bar{v}$ is the mean thermal speed of the gas being transported $[(8kT/\pi m)^{1/2}]$, k is Boltzmann's constant, T is the absolute temperature, m is the molecular mass, and Δp is the pressure difference across the ends of the annulus.

Table I gives the transmission probability Q for some selected values of σ and L .

These results have been checked in the limits $\sigma \rightarrow 0$ and $\sigma \rightarrow 1$ when one expects Q for the annulus to approach that for a capillary and for the flow between flat plates respectively. The transmission probabilities for these two systems have been given in the previous note,¹ and the annulus results were found to reduce to the capillary and flat plate results in the limiting cases.

The Monte Carlo technique used by Davis⁵ for calculating Q requires relatively large amounts of computer time and this disadvantage increases with increasing L . Consequently comparison with his results only extends up to an L of 20, the maximum L for which he published results. Table II indicates the excellent agreement between the Monte Carlo results and the upper bounds obtained by the variation technique.

For practical use, an empirical equation has been obtained which reproduces the variational results with a maximum error of about 1.5%. This maximum error occurs for values of σ close to unity.

TABLE I. Transmission probability of an annulus ($Q \times 10^4$) radius ratio, σ .

L	0.1	0.2	0.4	0.6	0.8	0.95
0.5	8017	8022	8030	8037	8043	8046
1.0	6737	6754	6783	6808	6829	6842
1.5	5842	5867	5915	5958	5997	6020
2.0	5175	5206	5266	5324	5378	5413
2.5	4655	4690	4758	4826	4894	4940
3.0	4237	4274	4348	4423	4501	4558
3.5	3893	3931	4007	4087	4174	4241
4.0	3604	3642	3720	3804	3896	3972
5.0	3123	3181	3260	3347	3448	3538
6.0	2791	2828	2906	2994	3100	3201
7.0	2513	2548	2625	2712	2820	2929
8.0	2286	2321	2395	2481	2589	2704
9.0	2099	2132	2204	2288	2396	2515
10.0	1941	1973	2042	2124	2230	2352
15	1414	1440	1499	1569	1666	1792
25	921.7	941.1	984.5	1038	1116	1230
50	496.0	507.6	533.9	567.4	618.2	700.4
100	258.9	265.4	280.1	299.2	328.9	380.5
200	132.7	136.1	144.0	154.3	170.6	200.1
500	53.97	55.40	58.69	63.04	70.00	82.99
10 ³	27.15	27.88	29.56	31.77	35.34	42.09
10 ⁴	2.733	2.807	2.978	3.204	3.570	4.273
10 ⁶	0.2735	0.2809	0.2980	0.3207	0.3575	0.4282

TABLE II. Comparison of transmission probability by variation and Monte Carlo methods.

Radius ratio σ	Length/spacing L	Transmission Probability, Q	
		Variation method	Monte Carlo method
0.25	4.0	0.3661	0.362±0.007
	8.0	0.2339	0.233±0.006
	16.0	0.1381	0.134±0.010
0.5	2.0	0.5295	0.524±0.007
	4.0	0.3761	0.360±0.007
	6.0	0.2948	0.289±0.006
	8.0	0.2436	0.238±0.006
	10.0	0.2081	0.203±0.006
	12.0	0.1819	0.177±0.012
	14.0	0.1617	0.162±0.011
	16.0	0.1456	0.146±0.011
	18.0	0.1325	0.136±0.010
	20.0	0.1216	0.124±0.010
0.75	2.0	0.5365	0.541±0.007
	4.0	0.3872	0.388±0.007
	6.0	0.3071	0.305±0.007
	8.0	0.2559	0.252±0.006
	10.0	0.2200	0.217±0.006
	12.0	0.1933	0.193±0.006
	16.0	0.1559	0.145±0.011
	20.0	0.1310	0.128±0.010
0.90	2.5	0.4926	0.488±0.007
	5.0	0.3507	0.351±0.007
	10.0	0.2304	0.230±0.006
	15.0	0.1740	0.173±0.005
	20.0	0.1404	0.144±0.008
	25.0	0.1180	0.123±0.008
	30.0	0.1019	0.102±0.007
	35.0	0.0897	0.094±0.007
	40.0	0.0802	0.083±0.006

The equation and its range of validity is

$$0 \leq L \leq 100$$

$$Q = \{1 + L[0.5 - A \tan^{-1}(L/B)]\}^{-1},$$

$$0 \leq \sigma \leq 0.9,$$

where

$$A = (0.0741 - 0.014\sigma - 0.037\sigma^2) / (1 - 0.918\sigma + 0.050\sigma^2),$$

$$B = (5.825 - 2.86\sigma - 1.45\sigma^2) / (1 + 0.56\sigma - 1.28\sigma^2).$$

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Electrical Transport Properties in the Pseudobinary System NbO₂-VO₂

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We wish to report measurements of the electrical conductivity, the thermoelectric power and the Hall effect on some alloys in