this cooling cycle. Such conditions could conceivably explain the cubic morphology of reported (*17*) cliftonite (graphite) particles; yet other postulates may explain the formation of cliftonite (*11, 12*).

Since the moon suffers many highly energetic impacts, unattended by atmospheric friction, one may expect to find shock-formed hexagonal and cubic diamonds on its surface.

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Molecular Beams with Energies above One Electron Volt

Abstract. *By using as sources supersonic jets of hydrogen or helium containing small concentrations of heavier molecules we have been able to obtain molecular beams with kinetic energies of the heavy molecules well into the range above 1 electron volt. A variety of molecules have been successfully accelerated. Intensities of 10^{16} to 10^{17} heavy molecules per steradian-second have been achieved at these high energies.*

In the usual molecular-beam apparatus, gas effuses from a source cavity or "oven" through a small hole into a chamber maintained at high vacuum by continuous pumping. The gas in the oven is maintained at a density sufficiently low that the molecules undergo no collisions in passing through the hole. Once in the evacuated chamber they travel in straight-line continuations of their original trajectories until they strike a surface and lose their identity in the background gas. If one or more collimating orifices are placed coaxially with the source hole, those molecules having trajectories within the solid angle defined by the source and collimating apertures emerge from the last collimator in the form of a beam or ray. This collision-free beam of molecules may be subjected to deflection by various kinds of fields. Or these molecules may be directed at various kinds of targets (such as surfaces and intersecting beams of electrons, ions, photons, or other molecules) resulting in collisions under highly specified and controlled conditions. Both deflection and collision experiments have been a source of information about the structure and properties of atoms and molecules (*1*) and have led to such important technological developments as the atomic clock, the maser, and the laser.

In collision experiments relating to chemical reactions and structure, molecular beams play a role analogous to the more familiar one performed by particle beams from high-energy accelerators in the study of nuclear reactions and structure. Molecular beams have suffered from limitations in energy and intensity which are analogous to the limitations encountered by their more famous high-energy cousins (*2*). Effusive sources of the type we have described are very often incapable of providing beam intensity sufficient to give useful signal-to-noise ratios in experiments involving collisional events that have small cross sections or probabilities of occurrence. Perhaps even more important has been the energy limitation. With the refractory materials now available, source ovens have a maximum operating temperature of about 3000°K which corresponds to an upper limit in mean kinetic energy of the beam of about 12 kcal per mole or 0.5 ev per molecule. Beams formed by charge-exchange neutralization of electrostatically accelerated ions have essentially no upper limit to their energy but because of space-charge effects cannot provide the intensities necessary for many experiments at energies below 10 ev. Consequently, the range from 0.5 to 10 ev has been virtually inaccessible to molecular-beam experiments. In just this range occur the gas-phase collision processes important in many chemical reactions and in high temperature transport phenomena.

Kantrowitz and Grey in 1951 suggested that very large increases in useful beam intensity might be obtained if the quiescent gas in the usual oven source were replaced by a low-density supersonic jet (*3*). They reasoned that if the gas at the entrance to the source orifice or "skimmer" had a streaming velocity that was large relative to the random thermal velocity of the molecules, that is, if it had a high Mach number or speed ratio, the molecules passing through the skimmer would be "focused" on the beam axis by the high component of velocity in the beam direction. Since Becker and Bier reported the experimental substantiation of this idea (*4*), a number of groups have confirmed the effectiveness of the Kantrowitz-Grey technique for providing useful intensities thousands of times greater than those possible with effusive sources (*5*). We now report that the use of a supersonic jet as the source gas for a molecular beam permits increasing the beam energy into the hitherto inaccessible range above 0.5 ev.

If a pure gas expands isentropically in a free jet, the average kinetic energy of the molecules in laboratory coordinates due to their streaming motion is:

$$\tfrac{1}{2} mV^2 = \int_T^{T_0} c_p \, dT \qquad (1)$$

where V is the flow velocity, m is the molecular mass, c_p is the molecular specific heat at constant pressure, T_0 is the stagnation or source temperature, and T is the static temperature in the jet. At Mach numbers above 5 the static temperature becomes effectively zero and the average kinetic energy of the molecules rapidly approaches a limiting value which is slightly larger than the average kinetic energy in an effusive beam having the same source temperature. In the case of a binary

gas mixture of light and heavy molecules, if there are enough collisions to insure temperature and velocity equilibration between the species during the expansion, Eq. 1 will apply, but m and c_p must be given their concentration-weighted mean values. For expansion to high Mach number the kinetic energy of the heavy species is given by:

$$\tfrac{1}{2} m_h V^2 = \frac{m_h}{m_m} \int_0^{T_0} c_{pm} dT \qquad (2)$$

where the subscript m indicates the mean value for the mixture and h indicates the heavy species. If differences in specific heats are neglected, it is clear that for the case of a "solution" of heavy species in a light carrier gas the translational kinetic energy of the heavy species will be higher than that of a pure gas by the factor m_h/m_m which in a very dilute solution approaches the ratio of the molecular masses of the heavy and light species. Thus, for a 1 percent solution of argon in helium the argon molecules would have energies approaching ten times the value they would have if pure argon were expanded from the same source temperature.

The idea then is that a gas mixture comprising a small concentration of heavy species in a light carrier be expanded in a jet to form a molecular beam source in accordance with the Kantrowitz-Grey principle. Of course, if the source gas contains only a small concentration of the heavy species the intensity of the latter in the final beam will suffer. However, the total intensity obtainable with a supersonic jet source is so large that the net intensity of heavy species should still exceed that which can be realized with an effusive source of pure gas. Moreover, as it turns out, the heavy molecules are "focused" on the beam centerline more effectively than the light molecules so that the ratio of heavy species to light in the final beam is greater than in the source gas by the factor m_h/m_l, the ratio of heavy to light (l) molecular masses. Indeed, there would seem to be no difficulty with respect to net intensity in the use of gas mixtures to obtain high energy beams but rather a problem of whether the presence of light species in the beam might give rise to noise or interference effects. Mass-discriminating detectors would seem capable of overcoming this problem in many experiments. The main uncertainty in the general idea has been whether velocity equilibration between the species could be obtained at jet densities low enough to permit extraction of a beam.

The first indication that such gas dynamic acceleration of heavy species by a light carrier gas to obtain high beam energies is feasible was provided by velocity measurements with argon-hydrogen mixtures by Becker and Henkes (*6*). Klingelhofer and Lohse have also accelerated argon with hydrogen but the energy which they achieved (from a room temperature source), 1.1 ev, was somewhat lower than expected (*7*). Recently, we have demonstrated experimentally that gas dynamic acceleration works as well as had been hoped for a wide variety of species and over a wide range of source temperatures.

We used a time-of-flight technique to determine the velocities and, therefore, the translational kinetic energies of the molecules in a beam extracted from a supersonic jet. In this method, the beam is chopped into short segments by a rotating shutter and the time of flight of the segments to a downstream detector is measured (*9*). The only question that arises in the case of gas mixtures concerns the ability of the detector, a simple flow-through ionization gauge, to "see" the heavy species in the presence of the light carrier gas. Actually, the ionization cross section for the heavy species is much greater than for the light species. Also the results agree with theory as expressed in Eq. 2. In addition, when there is appreciable "slip" or velocity difference between the species the individual species velocities can be distinguished. For these reasons, there seems to be no doubt that the results we report here relate to the heavy species. This question has already been treated in some detail (*10*).

In Fig. 1 are shown velocities obtained with helium-argon mixtures. The points are measured values. The solid curve represents theoretical values computed from Eq. 2. The agreement between theory and experiment is within experimental error, about 1 percent in all cases. For these measurements the source pressure was 1536 torr, source temperature was 300°K, the nozzle di-

Table 1. Velocities and kinetic energies obtained in molecular beams from supersonic jets of carrier gas containing 1 mole percent of solute.

Solute	Helium carrier					Hydrogen carrier				
	T_0 (°K)	P_0 (torr)	V_{obs} (10^5 cm/sec)	V_{obs}/V_{th}	$\frac{1}{2}m_hV^2$ (ev)	T_0 (°K)	P_0 (torr)	V_{obs} (10^5 cm/sec)	V_{obs}/V_{th}	$\frac{1}{2}m_hV^2$ (ev)
CH_4	300	100	1.70	0.98	0.24	300	100	2.49	0.95	0.51
	1200	285	3.47	1.00	1.00	900	200	4.39	.91	1.59
NH_3	300	150	1.70	0.98	0.25	300	150	2.55	0.97	0.57
N_2	300	100	1.68	0.98	0.41					
	1200	150	3.36	.98	1.64					
CO	300	150	1.67	0.97	0.40	300	150	2.40	0.94	0.83
	900	225	3.05	1.03	1.35	900	200	4.18	.89	2.52
	1200	250	3.40	0.99	1.67					
C_2H_4	300	150	1.66	0.97	0.40	300	150	2.51	0.98	0.91
	1200	250	3.40	.99	1.67	1150	250	4.58	.87	3.04
C_2H_6	300	100	1.69	0.99	0.44	300	100	2.46	0.97	0.94
	900	225	2.99	1.01	1.39	900	200	4.14	.89	2.65
H_2S	300	150	1.71	1.00	0.51	300	150	2.39	0.95	1.00
	1180	225	3.36	0.99	1.98	1070	175	4.20	.83	3.10
C_3H_6	300	150	1.68	0.99	0.61	300	100	2.21	0.89	1.06
	900	225	2.94	1.01	1.88	900	215	3.89	.85	3.29
C_3H_8	300	100	1.65	0.98	0.62	300	100	2.25	0.91	1.15
	900	225	2.88	.99	1.88	900	200	3.84	.85	3.36
CO_2	300	200	1.67	0.99	0.63	300	150	2.25	0.91	1.15
	1440	250	3.70	1.00	3.11	900	225	3.80	.84	3.28
N_2O	300	200	1.68	1.00	0.68	300	150	2.30	0.93	1.20
	1200	225	3.09	0.91	2.18					
C_4H_{10}	300	100	1.62	0.98	0.76	300	100	2.20	0.92	1.45
	900	225	2.85	1.00	2.44	900	200	3.70	.84	4.10
SO_2	300	200	1.61	0.98	0.86	300	150	2.24	0.95	1.66
	1200	250	3.11	.95	3.20	955	200	3.54	.79	4.01
CH_3Br	300	150	1.51	0.95	1.12	300	150	2.00	0.89	1.96
	1155	225	2.82	.91	3.90	1155	225	3.42	.74	5.75
Xe	300	200	1.40	0.92	1.33	300	150	1.82	0.86	2.25
						2050	175	3.25	.53	7.17
SF_6	300	150	1.38	0.91	1.44	300	150	1.77	0.85	2.37
	1150	275	2.56	.87	4.95	1180	250	2.94	.67	6.53

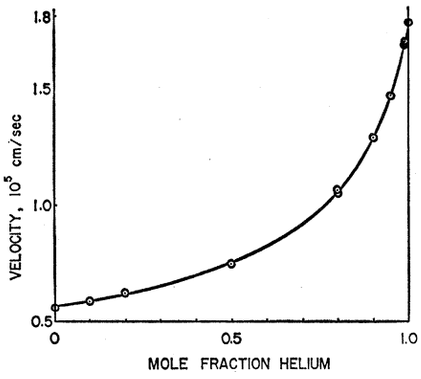

Fig. 1. Effect of composition on velocities obtained in molecular beams formed with helium-argon mixtures.

ameter was 0.1 mm, the diameter of the first collimating orifice or skimmer was 0.77 mm, and the distance from nozzle to skimmer was 19 mm.

The results for a number of different gas mixtures comprising 1 percent of the solute or heavy species in either helium or hydrogen as the carrier gas are shown in Table 1. The nozzle diameter was 0.51 mm, the skimmer size and location were as described above. We computed the theoretical velocities from Eq. 2 assuming no contribution to specific heat by the solute except for translational energy. We have found that rotational energy of hydrogen does not relax completely during expansion. Nevertheless, theoretical values for the hydrogen mixtures were computed on the basis of complete relaxation.

In most cases the observed velocities are very close to the theoretical values. The departures become significant only for the very heavy species. We have found that the "slip" indicated by such departures can be overcome by increasing source density (*10*). The important feature of the results in Table 1 is the fact that the solute kinetic energies go well into the energy range above 0.5 ev. The highest values are realized, of course, with the highest source temperatures. We have used source temperatures up to about 2100°K, but there should be no great difficulty in going higher. In fact, unlike oven sources, nozzle sources can provide source gas temperatures above the melting point of the construction material because the high density of the gas permits cooling the nozzle to temperatures below that of the gas. This possibility has led to the use of shock tubes and electric arcs to achieve very high source-gas temperatures. The main temperature limitation would seem to be determined by the thermal stability of the solute species. In fact, in some of the cases in Table 1 there may have been reaction or decomposition of the solute in the source.

We have also measured the intensities of the beams obtained in these experiments. For this purpose we used an ionization gage manometer described previously (*11*). The results are not quite as unambiguous as for the velocity measurements, because the contribution of the carrier gas to the gage signal cannot be quite so safely taken into account. It appears that the intensities of the heavy species are approximately those predicted by Kantrowitz-Grey theory. In any event, there is no doubt that intensities of the heavy species of 10^{16} to 10^{17} molecules per steradian-second were obtained in these experiments. Higher values might be achieved by increases in source pressure and skimmer area.

There remain some possible problems in the use of gas dynamic acceleration of heavy species to obtain high kinetic energies from the beam. With low source temperatures and high boiling solutes there exists the possibility of condensation of the heavy species in the jet. There are also situations in which there is uncertainty as to the internal energy states of the accelerated molecules. Nevertheless, in view of the results reported here the way now seems open to contemplate molecular beam experiments at energies substantially higher than have heretofore been possible.

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Potassium:Argon Dating of Iron Meteorites

Abstract. *The potassium:argon age of the metal phase of Weekeroo Station iron meteorite, determined by neutron-activation analysis, is about 10^{10} years; it is similar to ages previously measured for other iron meteorites, but distinctly disagrees with a strontium:rubidium age of 4.7 × 10^9 years measured by other workers on silicate inclusions in this meteorite.*

The formation or solidification ages of iron meteorites have never been well determined. The most direct method seems to be that of Stoenner and Zähringer (*1*), who measured the potassium and argon contents by neutron-activation analysis. Their data, however, indicated ages of from about 7 to 10 × 10^9 years, whereas the age of the solar system is generally well accepted at about 4.7 × 10^9 years. Fisher (*2*) later confirmed these data, but concluded that they were evidence of an unexplained potassium:argon anomaly rather than that they indicated true ages. From Müller and Zähringer's (*3*) more recent data they conclude that a potassium:argon age of about 6.3 × 10^9 years can be assigned to many iron meteorites.

Wasserburg, Burnett, and Frondel's (*4*) recent determinations of the strontium:rubidium age of silicate inclusions in Weekeroo Station iron meteorite indicated 4.7 × 10^9 years; they therefore concluded that, if their data could be applied to iron meteorites in general, the great potassium:argon ages observed in iron meteorites are misleading. But at least one iron meteorite has been shown to have a potassium:argon age of less than 4.7 × 10^9 years (*5*); so it was necessary to measure directly the potassium:argon age of the metal phase of Weekeroo Station. In the experiment reported here we have used samples generously provided by Wasserburg, Burnett, and Frondel from the slab on which their strontium:rubidium work was done.

Our experimental technique resembled an earlier one (*5*), with the major