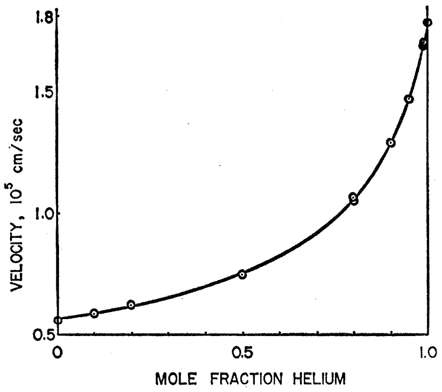

Fig. 1. Effect of composition on velocities obtained in molecular beams formed with helium-argon mixtures.

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.

N. ABUAF, J. B. ANDERSON
R. P. ANDRES, J. B. FENN
D. G. H. MARSDEN
Beam Kinetics Laboratory, School of Engineering and Applied Science, Princeton University, Princeton, New Jersey

References and Notes

1. N. F. Ramsey, *Molecular Beams* (Oxford Univ. Press, New York, 1956); J. Ross, Ed., *Advances Chem. Phys.* **10** (1966); R. B. Bernstein, *Science* **144**, 141 (1964).
2. J. B. Anderson, R. P. Andres, J. B. Fenn, in *Advances At. Mol. Phys.* **1**, 345 (1965).
3. A. Kantrowitz and J. Grey, *Rev. Sci. Instr.* **22**, 328 (1951).
4. E. W. Becker and K. Bier, *Z. Naturforsch.* **9a**, 975 (1954).
5. E. L. Knuth, *Appl. Mech. Rev.* **17**, 751 (1964); J. B. French, *Amer. Inst. Aeron. Astronaut. J.* **3**, 993 (1965); J. B. Anderson, R. P. Andres, J. B. Fenn, in *Advances Chem. Phys.* **10**, 275 (1966).
6. E. W. Becker and W. Henkes, *Z. Physik* **146**, 320 (1956).
7. R. Klingelhofer and P. Lohse, *Phys. Fluids* **7**, 379 (1964).
8. J. B. Anderson and J. B. Fenn, *ibid.* **8**, 780 (1965).
9. N. Abuaf *et al.*, in *Recent Advances in Aerothermochemistry* [Proc. Third AGARD (Advisory Group for Aeronautical Research and Development of North Atlantic Treaty Organization) Colloquium, Oslo, 1966], in press.
10. N. Abuaf, J. B. Anderson, R. P. Andres, J. B. Fenn, D. R. Miller, in *Rarefied Gas Dynamics*, C. L. Brundin, Ed. (Academic Press, New York, in press).
11. J. B. Anderson and M. Boudart, *J. Catalysis* **3**, 216 (1964).

14 November 1966

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

Table 1. Potassium and argon data. Abbreviations: *r*, radiogenic; *p*, primordial.

Weekeroo Station sample		Nuclide			Age ($\times 10^9$ yr)
No.	Weight (g)	Content ($\times 10^{12}$ atom/g)		Ratio ($Ar^{40}_r : K^{40}_p$)	
		Ar^{40}	K^{41}		
K-1	1.4032	30.3 ± 1.9	1540 ± 70	9.6 ± 1.7	8.5 + 0.2, − 0.4
K-2	1.3260	8.0 ± 0.8	215 ± 20	15.4 ± 3.1	9.3 ± 0.4
B-1	1.1880	17.2 ± 2.3	2370 ± 200	3.4 ± 0.7	6.5 ± 0.4
G-1	1.1653	22.8 ± 1.7	410 ± 30	26.8 ± 4.5	10.4 + 0.3, − 0.4

Table 2. Mass-spectrometric data.

Weekeroo Station sample	Data [$\times 10^{-8}$ (standard) cm^3/g]					
	He^3	He^4	Ne^{21}	Ne^{22}	Ar^{36}	Ar^{38}
K-92	480	1610	5.24	5.73	17.2	27.2
K-94	482	1560	5.25	5.71	17.8	28.4
K-98	462	1560	5.13	5.40	17.1	26.8
B-94	498	1660	5.79	6.12	19.1	30.4

exception that the meteorite samples were dissolved in HNO_3 rather than melted. Helium gas was bubbled through the dissolving solution and, together with carrier and meteoritic argon, was swept through a vacuum line. The argon was trapped on charcoal at liquid-nitrogen temperatures, purified over hot titanium, and pumped directly into a Geiger counter. The 1.8-hour Ar^{41} activity was followed down to background. Potassium was precipitated from the final solution, together with carrier, chemically purified, and counted as the tetraphenyl boron. The 12.4-hour K^{42} activity was followed down to background. Typical counting rates for both K^{42} and Ar^{41} were tens of counts per minute; background was 7 to 15 count/min. Before irradiation the samples were lightly etched to remove surface contamination; loss of potassium during this etching, shown to have been less than 15 percent, will be discussed in detail in a later publication. The data appear in Table 1.

Small samples were cut from those on which these measurements were made and were analyzed separately, for the cosmogenic (*c*) rare gases, by mass spectrometry according to well-established procedures. Table 2 shows no apparent anomalies; thus from these data we can calculate the amounts of cosmogenic Ar_c^{40}, K_c^{40}, and K_c^{41}, utilizing the production ratios determined earlier (*6*): Ar_c^{40}, 1.5×10^{12} atom/g; K_c^{40}, 11×10^{12}, and K_c^{41}, 6.4×10^{12}. Then, by correcting the raw data of Table 1 for cosmogenic Ar^{40} and K^{41} and for cosmoradiogenic Ar^{40} (from the decay of cosmogenic K^{40}), and by assuming the terrestrial K^{40}:K^{41} ratio for primordial potassium (*7*), potassium:argon ages can be calculated (Table 1).

The ages found by us are typical of the great ages found for most iron meteorites. From these, in conjunction with the strontium:rubidium data of Wasserburg *et al.* (*4*) on silicate inclusions in this meteorite, we conclude that the potassium:argon dating technique as applied to iron meteorites gives unreliable results. One may derive *ad hoc* possible explanations of the discord between the silicate and iron-phase ages, such as shock emplacement of these inclusions within the metal matrix without disturbing the potassium: argon ratios in the metal, but we feel that such mechanisms are unlikely.

L. RANCITELLI
Cornell University, Ithaca, New York
D. E. FISHER
Institute of Marine Sciences,
University of Miami, Miami, Florida
J. FUNKHOUSER
O. A. SCHAEFFER
State University of New York,
Stony Brook

References and Notes

1. R. W. Stoenner and J. Zähringer, *Geochim. Cosmochim. Acta* **15**, 40 (1958).
2. D. E. Fisher, *J. Geophys. Res.* **70**, 2445 (1965).
3. O. Müller and J. Zähringer, *Geochim. Cosmochim. Acta*, in press.
4. G. J. Wasserburg, D. S. Burnett, C. Frondel, *Science* **150**, 1814 (1965).

→ D. E. Fisher, *ibid.* **139**, 752 (1963).

6. P. Lammerzahl and J. Zähringer, *Geochim. Cosmochim. Acta*, in press; J. R. Arnold, M. Honda, D. Lal, *J. Geophys. Res.* **66**, 3519 (1961).
7. D. S. Burnett, H. J. Lippolt, G. J. Wasserburg, *J. Geophys. Res.* **71**, 1249 (1966).

8. Aided by AEC contracts AT-(30-1)-2794 and AT-(30-1)-3629. We thank G. J. Wasserburg, D. S. Burnett, and C. Frondel for samples of Weekeroo Station, and J. Taylor for assistance with the rare-gas measurements. Publication No. 767 of the Institute of Marine Sciences.

12 December 1966

Radiation of Hemocyanin: Inactivation and Reactivation of Oxygen-Carrying Capacity

Abstract. *Oxygen-carrying capacity of hemocyanin from* Limulus *and* Busycotypus (Busycon) *decreases with increasing radiation, giving initial yield values for* $G(-O_2)$ *of 1.1 and 1.0, respectively. High radiation doses regenerate this capacity of* Busycotypus *hemocyanin. These effects are attributed largely to the dual nature of hydrogen peroxide, which, at low concentrations, oxidizes protein-bound copper and at high concentrations, that is, at high doses, reduces oxidized copper. The ability of hemocyanin to decompose hydrogen peroxide is relatively unaffected by irradiation, which suggests that copper atoms at the active sites are not all equivalent. The catalase-like activity of* Busycotypus *hemocyanin can be simulated by amino acid chelates of copper, including arginine, histidine, and glycine.*

Hemocyanin is a nonheme oxygen-carrying copper protein found in the hemolymph of terrestrial and marine invertebrates (*1, 2*). It reacts reversibly with molecular oxygen at relatively high partial pressures and releases oxygen to tissues where the partial pressure is low. One molecule of oxygen combines stoichiometrically with two atoms of copper in hemocyanin, and it appears that the active site involves a pair of copper ions bridged by an oxygen molecule (*3*). Deoxygenated hemocyanin contains copper only in the cuprous state, while oxygenated hemocyanin contains cupric ions in what might be described as a state favoring rapid electron transfer (*1, 3*). Because of the very important and special role of oxygen in radiobiological damage and protection (*4, 5*), hemocyanin serves as a useful model for studying the effects of ionizing radiation on oxygenation reactions (*6*), particularly in view of the suggestion (*7*) that a contributory mechanism of radiobiological damage involves interference with the ability of copper-containing oxidases to interact with molecular oxygen. Presumably, radiation-induced oxidation of protein-bound copper to the cupric state leads to inhibition of oxygenation reactions and energy utilization.

Early investigators (*8–10*), who studied the actions of ionizing radiation on hemocyanin used, as criteria of radiation damage, rupture of the copper-protein bond or dissociation of pro-