A Molecular Beam Apparatus for Student
Experiments on Reactive Scattering*

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Introduction

The properties of substances and the chemical reactions which occurs between them often become simpler to understand when they are studied on a molecular rather than a macroscopic scale. One approach to this kind of simplification in chemical kinetics is the use of scattering theory and of experiments with molecular beams to learn about the interactions of individual molecules.

Some consideration of elastic, inelastic, and reactive scattering in the teaching of undergraduate courses has been advocated as a useful part of physical chemistry (1) following naturally after the usual treatments of kinetic theory. Discussions of molecular beam experiments on reactive scattering appear in current freshman textbooks. There has also been a description of a simple apparatus for the production of a molecular beam of sulfur vapor which is detected by its reaction with a hot copper surface (2). No scattering was studied in this experiment, but it was done with homemade apparatus. Nevertheless, there is a widespread impression that scattering experiments are exorbitantly expensive and complex, perhaps

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out-of-the-question for undergraduate chemistry courses.

The purpose of this paper is to describe the construction and operation of a simple molecular beam apparatus, which has been used by undergraduates in experimental projects on reactive scattering, and to show some of the results which have been obtained with it for the reactions

and

Apparatus

The apparatus produces directed beams of an alkali metal, such as K, and a reactive collision partner such as Br_2 or CH_3I which has a vapor pressure of about 10^{-2} mm⁻² (a. torr) or more at room temperature. The speeds of the molecules in the beams are distributed over the ranges corresponding to equilibrium conditions in the beam sources, i.e. there is no velocity selection. Figure 1 is a schematic drawing of the various components mounted inside the vacuum system (the lower case letters identify the components). The wiring diagram is given in Figure 2. The main vacuum chamber is a vertical, brass cylinder (j in Fig. 1) 13 cm high and 15 cm in diameter evacuated by a 5 cm diffusion pump (x), connected in series with a mechanical forepump. Further pumping of the condensable material of the beams is provided by liquid-nitrogen cooled

shields (k and s). The K beam emerges from a hole (n) of 0.25 mm diameter in a stainless steel oven (l) sealed by pressing in a tapered brass plug (l'). The oven is heated by a coil of Ta wire (m) of 0.25 mm diameter and resistance 0.5 Ω wrapped around an Al_2O_3 cylinder (not shown). The K beam is collimated by a slit (p, 2.3 mm high by 0.4 mm wide) in shield (o) and then intersects the second beam at a right angle. This second beam is produced at a constant vapor pressure from a sample held at a fixed temperature in a Dewar (a) outside the vacuum chamber, enters the chamber through a vertical tube (q), flows through a thin stainless-steel tube (q'), and finally emerges into the vacuum through an array of glass capillaries (r; each capillary is 0.8 mm long and 0.05 mm in diameter) sealed to the end of q' by epoxy cement. The two beams turn as a unit when the support tube (q) is rotated from outside the system. This tube is fastened to part of a sextant (shown schematically as f) which permits rapid and accurate angle settings. Scattered molecules leaving the region of intersection of the two beams in the proper direction pass a shutter (not shown), move through a slit (t; 10 mm high by 3.4 mm wide) and hit one of the two ribbon shaped filaments (Pt: 30 mm x 0.5 mm x 0.025 mm; W: 30 mm x 0.5 mm x 0.012 mm). When the filaments are hot (dull red) both K and K halides form K^+ ions on W while only K forms K^+ on Pt (3). Thus the incoming fluxes of both K and KBr can be measured by recording the

current from the W filament and the difference between the currents from the W and Pt filaments respectively. Use of the shutter permits a distinction between molecules in the beams and those which may come from impurities in the filaments or background of K near the detector.

Although the pressure in the main chamber is not measured directly, the quality of the vacuum can be determined satisfactorily from the foreline pressure read on a thermocouple gauge (y). When this pressure rises no more than about 0.1 N m^{-2} (a few microns) per minute with the trap (h) cooled with liquid nitrogen and with the valve (g) closed and the beams both on, the leaks are negligible. An unsatisfactory vacuum is also indicated when the cross beam is not on but scattering from the residual gas in the chamber makes the width of the K beam significantly greater than the normal value (shown in Fig. 3).

Figure 1 is intended only to show the general arrangement of the apparatus. Those who may wish more information on the details of the construction or the suppliers for the materials can obtain it by writing to the authors. The machining and hard soldering for the vacuum system and the components took about 40 hours of shop time. The most important piece of commercial equipment needed is the electrometer. The results described here were obtained using a Keithley Model 610B (\$565). The diffusion pump, the mechanical

pump, the thermocouple gauge and control unit, and the two power supplies are standard items which cost approximately \$750 if they must be bought new. Some of the parts needed in small quantities such as the Ta, Pt and W wire and the electrical feed throughs can be ordered separately or perhaps be contributed by a well stocked laboratory. The total cost for the assembled apparatus is approximately \$1700.

Experimental Procedure

To prepare for a run about 3 mm³ of K is rinsed with a hydrocarbon solvent and placed in the heatable oven; about 1 cm³ of the material for the cross beam is placed in the glass reservoir (b) with cap (c). Next, the system is evacuated, and the liquid nitrogen trap is filled. Air is removed from (b) by freezing the sample in liquid nitrogen and then opening stopcock (d). The Pt and W filaments are cleaned by heating in vacuum to a yellow-white color as viewed through window j. The background ion current from the filaments decays rapidly ($\approx$ 1 hour) to a satisfactory value which is $\approx 10^{-11}$ A at the operating temperatures (1300°K, red-orange for the W, 1.2V, 0.5A; 1500°K, yellow for the Pt, 2.0V, 1.05A). The filament temperatures were measured with an optical pyrometer but may be set approximately by eye. The Pt filament detects both K and KBr or KI if it has been heated in O₂ (4). To reduce its sensitivity to the halides, the Pt filament is heated for a few minutes (yellow color) in a hydrocarbon vapor at a low pressure (approximately 10⁻³ mm⁻² or 10⁻⁵ torr). Frequently the diffusion pump oil is present in the chamber at

a high enough pressure, if the trap is not cooled, to serve this purpose. Silicone oil should be avoided for the diffusion pump since its use may keep the Pt filament sensitive to the halides. The poisoning of the Pt for halide detection can be checked by making a beam of KBr or KI and comparing the signals on the two filaments.

To produce the K beam the horizontal part of the K oven is heated to about 300°C (the oven winding is dull red, 12V, 1.0A) while the liquid K remains at a lower temperature in the lower arm of the T. This keeps the K from clogging the exit hole (n). After about 20 minutes when the K beam is steady, the cross beam reservoir is surrounded by a constant temperature bath consisting of a liquid-solid mixture to maintain the vapor pressure of the cross beam at an appropriate value. For CH_3I a bath of CHCl_3 (M.P. -63.5°C) and for Br_2 a bath of CCl_4 (M.P. -23°C) were satisfactory in giving attenuations of the K beam of about 10% when stopcock (d) was opened. The two phase mixture was prepared by slowly adding liquid nitrogen to the liquids.

The measurement of an angular distribution of the scattered intensity $I(\alpha)$ takes about 10 minutes. This is typically done by starting with the main beam, the angle of maximum intensity α_{MB} , going in steps to the maximum angle, and then returning to α_{MB} . Averaging the two readings at each angle, α , provides a correction for a drift of the beam intensities with time. At each α the readings $I(\alpha)$ are the differences in the electrometer current with the shutter open and closed. To allow for slight differences in the efficiencies with which

the ions are formed on and collected from the two filaments, the Pt and W angular distributions are normalized to each other at angles near the K beam, α_{KB} .

Results

When the cross beam is off, the K is scattered only by the residual gases in the system and by surfaces on which the K does not condense completely. The readings on the W and Pt filaments are very nearly superposable as Fig. 3 shows. The beam width at 1/10 of maximum intensity is about 2.5° .

Figures 4 and 5 show the results when cross beams of Br_2 and CH_3I are used. In both cases the scattered signals from the two filaments I_W and I_{Pt} agree well near α_{KB} , but at larger angles I_W is larger than I_{Pt} . This difference, which is plotted in Fig. 6 is a measure of the angular distribution of potassium halide formed in the reaction. For reaction (1) the measured KBr flux is largest in the angular range $\alpha \lesssim 30^\circ$ while for reaction (2) the total amount of halide produced is much smaller for comparable attenuations of the K beam by the cross beam. The KI flux is largest for $50^\circ \lesssim \alpha \lesssim 90^\circ$. These results can be compared with those reported in the first studies of these reactions by Herschbach, Kwei and Norris (5) and by Wilson, Norris, Herm, Birely and Herschbach (6) and also those of other workers.

As is shown in these references the angular distributions can be interpreted with reference to kinematic diagrams such as those drawn in Fig. 7. Here the velocity vectors for the molecules in the two original beams $\vec{v}_K$ and $\vec{v}_m$, where m

is Br_2 or CH_3I , as well as that for the center of mass of the two molecules $\vec{v}_{\text{cm}}$ are plotted with a common origin. The relative velocity $\vec{v}$ is $\vec{v}_K - \vec{v}_M$. The magnitudes of the vectors are drawn to be proportional to the average speeds of the molecules in the vapor forming the beams, $v_i = \sqrt{\frac{8kT_i}{m_i}}$ where k is Boltzmann's constant, T_i is the absolute temperature of source i and m_i is the mass of beam molecule i . The temperatures are estimated to be 575°K for K and 300°K for Br_2 and CH_3I .

From the measured distributions of product, one can see that the KBr from reaction (1) is scattered forward (in the same direction with respect to the center of mass as that of the original K) while the KI from reaction (2) is scattered backward. In neither case is there scattering which is symmetric along $\vec{v}$ about the tip of $\vec{v}_{\text{cm}}$ as there would have to be if the complex formed by the reactants had existed as a unit for a time appreciably longer than it required to make one rotation (7). Further and more detailed interpretation of these and similar experiments can be found in many papers and reviews (8).

This demonstration that these reactions were direct, that is they did not proceed by forming a long-lived complex, was one of the first important chemical results from molecular beam experiments. Because neither fine angular resolution nor energy analysis of the product distributions is required for these experiments with reactive scattering, they can be done in a simple apparatus, such as that described here, and can provide a practical introduction to molecular beam studies.

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Figure Captions

1. Schematic drawing of molecular beam apparatus for reactive scattering with part of vacuum can (j) and cold shields (k) and (s) cut away to expose inner components. K beam source (l) and cross beam source (b) produce beams which intersect at the scattering center just below vertical inlet tube (q). Ions formed from the beam molecules hitting the filaments Pt and W are collected at (u) and form a current measured on an electrometer. The filament assembly is plugged into a base (u'). Plexiglass windows (i) permit direct observation of filaments and K oven and simplify the alignment of the components. Other components not identified in the text are: Swagelok right angle fitting (e) and clamp (g) holding sextant (f) to tube (q).
2. Wiring diagram for molecular beam apparatus.
3. $I(\alpha)$, angular distribution of flux of K recorded on W (O) and Pt (Δ) filaments in the absence of cross beam; Pt normalized to W near α_{MB} , angle of maximum $I(\alpha)$.
4. $I(\alpha)$, angular distribution of flux of K recorded on Pt(Δ) filament and of flux of K + KBr recorded on W(O) filament for K scattered from a cross beam of Br_2 ; Pt normalized to W near α_{MB} . 10% attenuation of K beam by Br_2 beam.
5. $I(\alpha)$, angular distribution of flux of K recorded on Pt(Δ) filament and of flux of K + KI recorded on W(O) filament for K scattered from a cross beam of CH_3I ; Pt normalized to W near α_{MB} .

6. Angular distribution of potassium halide $\Delta I(\alpha)$ divided by decrease of main K beam at $\alpha - \alpha_{MB} = 0$ when cross beam is turned on, $\Delta I(0)$. (O) KBr from reaction (1); (x) KI from reaction (2).

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7. Velocity vector diagrams for reactions (1) and (2). The angular range of the main flux of alkali halide is indicated in each case and neither shows a symmetric distribution of halide around the center of mass (tip of $\vec{v}_{cm}$). The arcs show locus of the tip of the relative velocity $\vec{v}$ for elastic scattering.

Fig. 1

Mechanical
Pump

Fig. 2

Fig. 3

FIG. 4

Fig. 5

Fig. 6

Fig. 7