

TABLE I. Coefficients for the inert gas repulsive potential curves.

Gas	A (eV)	B (Å) <sup>-1</sup>	Range applicable (Å)
He	2.19×10 <sup>8</sup>	5.40	1.83-2.17
Ne	3.77×10 <sup>6</sup>	7.72	2.25-2.57
Ar	4.04×10 <sup>9</sup>	8.21	3.00-3.19
Kr	2.02×10 <sup>12</sup>	9.44	3.26-3.44
Xe	1.62×10 <sup>15</sup>	10.37	3.69-3.79

mate functional form  $U(r) = A \exp(-Br)$  which reproduces the calculated repulsive potential energies with a maximum deviation of 4%. These deviations are always less than the estimated uncertainties in  $U(r)$ . The values of  $A$  and  $B$  are given in Table I.

In general, the new viscosity measurements agree with the potential function of Barker and Pompe,<sup>4</sup> which is based on second virial coefficients, molecular beam measurements, and theoretical calculations, in suggesting that the repulsive energy functions are less steep than earlier determinations of transport properties had indicated. This is illustrated for the case of argon in Fig. 1 where the older viscosity data<sup>5-7</sup> predict repulsive energies up to 100% greater than those obtained in this work, in keeping with earlier suggestions<sup>8,9</sup> that the older viscosity data is unreliable. The new results are in good agreement with recent thermal conductivity data.<sup>10,11</sup>

For helium the discrepancies are less marked and the results from both old<sup>5,6</sup> and new<sup>3</sup> viscosities agree with the potential function obtained from second virial coefficients<sup>1</sup> and the potential function proposed by Beck.<sup>12</sup>

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## Energy Requirements for Chemical Reaction: $H + HF \rightarrow H_2 + F^*$

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(Received 19 September 1969)

We report here the results of a classical trajectory study of the reaction  $H + HF \rightarrow H_2 + F$  restricted to

collinear motion. The results are similar to those reported by Polanyi and Wong<sup>1</sup> for exchange reaction on a hypothetical potential-energy surface having a barrier in the exit valley of the surface. Vibrational excitation of HF is found to be a necessary requirement for reaction at energies up to twice the barrier height.

The trajectory calculations were similar to those carried out by previous workers for other systems.<sup>2</sup> The potential-energy surface was a London-Eyring-Polanyi-Sato<sup>3</sup> surface (without overlap terms) modified to fit the triplet state energies for  $H_2$ . The triplet potential  $D_3$  for HF was adjusted to give a barrier height of 33.0 kcal for the collinear reaction favored by the surface. Figure 1 shows the surface with coordinates chosen to diagonalize the internal kinetic energy.<sup>4</sup> The reaction of H with HF is endothermic by 31.3 kcal (neglecting zero-point energies), an energy just 1.7 kcal less than the barrier height. The HF valley is intersected from the side by the  $H_2$  valley so that the requirement of vibrational motion of HF for reaction is not unexpected. Evidence that the surface is appropriate to the  $H + HF$  system is provided by three-dimensional calculations<sup>5</sup> for the reverse reaction which are in qualitative agreement with measurements of vibrational excitation of HF by Parker and Pimentel.<sup>6</sup>

The trajectories were calculated for HF in vibrational states  $v=0$  to  $v=4$  with relative initial kinetic energies of 1 to 70 kcal. For each set of initial state parameters, 10 trajectories were calculated with different initial vibrational phases.

The results, expressed as the fraction for each choice of  $v$  and kinetic energy, are shown in Fig. 2. No reaction was observed for  $v=0$  or  $v=1$  at translational energies up to 70 kcal mole. For  $v=2$  the onset of reaction with increasing translational energy occurred with total energy about 2 kcal above the minimum requirement. Above 20 kcal translational energy no reaction occurred. The onset of reaction for  $v=3$  and  $v=4$  occurred at about 3 kcal translational energy.

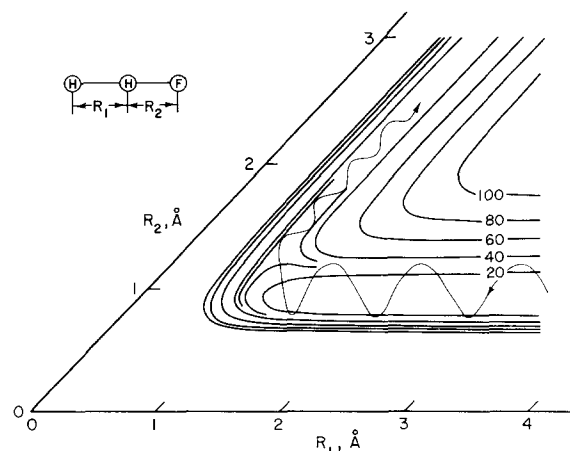


FIG. 1. Potential-energy surface for  $H-H-F$ . Contour lines for 30 and 35 kcal are unlabeled. A typical reaction path is shown.

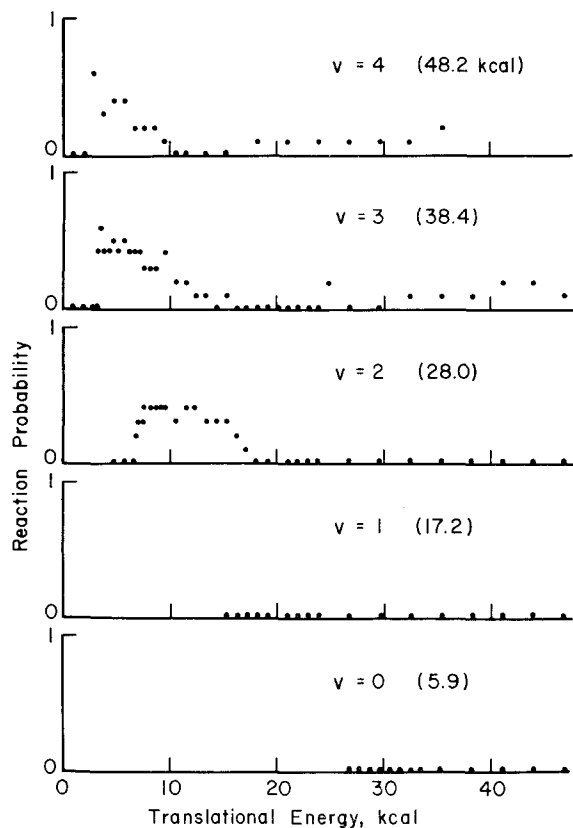


FIG. 2. Reaction probability as a function of initial translational energy for  $\text{H}+\text{HF}$  at the five lowest HF vibrational levels.

Reaction probability fell to zero at higher energies, then increased to 0.1 or 0.2 at still higher energies.

The over-all results may be interpreted in terms of the motion of a particle sliding on the potential-energy surface. Particles with high-translational energy alone are reflected back from the wall at the end of the HF valley. Vibrational energy is required for the particle to climb the side wall to the col. Increasing translational velocity decreases the probability of attaining a favorable vibrational phase while in the region of the col.

Parker and Pimentel<sup>2</sup> measured the chemical laser emission from vibrationally excited HF produced by the reaction  $\text{F}+\text{H}_2\rightarrow\text{HF}+\text{H}$  occurring with flash photolysis of  $\text{UF}_6$  in the presence of  $\text{H}_2$ . The ratio of the number of HF molecules produced with  $v=2$  to that for  $v=1$  was determined to be  $\sim 5.5$ . They conclude the data suggests that "for the reaction between HF and H the vibrational energy of HF is more effective than translational energy in bringing about this endothermic reaction." The results of the trajectory study support this conclusion. For the collinear system with a thermal energy distribution reaction must proceed almost exclusively via HF with  $v=2$ .

\* This work was supported by the National Science Foundation under Grant GK-4239.

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## Ignition of Benzene-Oxygen-Argon and Benzene-Oxygen-Nitrogen Mixtures by Shock Waves

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(Received 8 October 1969)

No data about the induction period for the oxidation of benzene in shock waves are available except those of Kogarko and Borisov.<sup>1</sup> They measured the induction period for 3%-benzene-97%-air mixtures and obtained the following relationship:

$$\tau = 10^{-13.6} \exp(-26\,200/T) \quad (1)$$

where  $\tau$  is induction period in seconds and  $T$  is shock temperature in degrees Kelvin. However, the dependence of  $\tau$  on the composition of the mixture was not

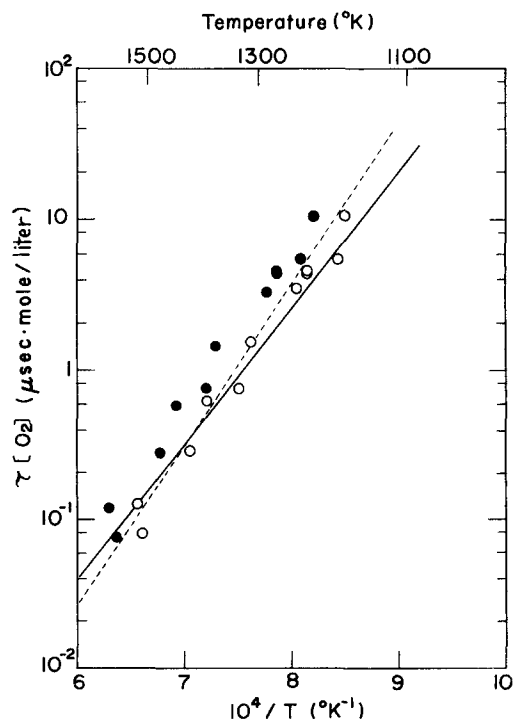


FIG. 1. Induction period vs reciprocal temperatures. Open circles correspond to case (a); solid circles, to case (b); solid line, to Eq. (2); and dotted line, to Eq. (1).