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FLUID MECHANICS LABORATORY

DEPARTMENT OF MECHANICAL ENGINEERING
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by

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# Gas Phase Recombination of Hydrogen

## A Comparison Between Theory and Experiment

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## ABSTRACT

The modified phase-space theory of reaction rates has been used to calculate the three-body recombination and dissociation rate coefficients of hydrogen in the presence of $H_2$, He, Ar, and Xe collision partners. The theoretical predictions, which rely on semi-empirically derived interatomic potential information, are shown to be in excellent agreement with the measured rate coefficients over wide temperature ranges.

## I. INTRODUCTION

The kinetics of the three-body recombination and dissociation of hydrogen in the presence of various collision partners, particularly $H_2$, has been quite extensively studied over the past several decades using flow-tube apparatus, flames, and shock tubes. Unfortunately, the general lack of agreement between the measurements within any one temperature range has rendered the task of assessing the merits of the corresponding dissociation and recombination rate theories rather difficult. However, by relying on the obvious preferences of some recent reviewers and active investigators,(1-6) we have concluded that reasonable limits can be set which bracket the probable values of the rate coefficients over limited temperature ranges. For instance, at room temperature ($\sim 300\ ^{o}K$) we believe that the more recent determinations(4-6) of the recombination rate coefficient for the $H + H + H_2$ system are probably the most accurate. Such a view sets the probable limits on the value of $k_r^{(H_2)}$ at about 4.7 and $9.4 \times 10^{-33}$ $cm^6$ $molecules^{-2}$ $sec.^{-1}$ The most recent measurements of $k_r^{(H_2)}$ by Ham, Trainor, and Kaufman(5) are of particular value because they show a clearly resolved temperature dependence over the range $77^{o}$ - $298^{o}K$, the duplication of which should be a crucial test of any recombination rate theory.

The high temperature shock-tube measurements of the dissociation rate coefficients also exhibit some variation between the different groups of investigators, but it is to be noted that of the six independent studies(7-12) of $k_d^{(H_2)}$ reported since 1961, the four most recent(9-12) give values which fall within the upper and lower bounds suggested by the careful measurements of Hurle, Jones, and Rosenfeld.(12) These bounds span a factor of about 2.5 at $3000^{o}K$ and increase to about a factor of 5 at the extreme temperature of $7000^{o}K$.

In previous publications(13, 14) we have compared the predictions of the modified phase-space theory of reaction rates with the experimental measurements for a variety of diatomic gases where the collision partner was a relatively inert argon atom. The success of the theory in correlating both the low temperature recombination rate measurements and high temperature dissociation rate measurements was quite substantial. Detailed discussions of the phase-space theory can be found in Keck's earlier work,(15) Rice's book,(16) and in the two references cited above. Our primary purpose in this paper will be to describe how we applied the theory to the reactions:

$$H + H + H_2 \underset{k_d^{(H_2)}}{\overset{k_r^{(H_2)}}{\rightleftharpoons}} 2\,H_2 \quad . \qquad (1)$$

In carrying out these calculations we have relied on theoretical quantum mechanical descriptions of the $H + H_2$ potential energy surface, semi-empirical descriptions, and molecular beam scattering measurements of H on $H_2$ obtained at thermal energies. Such information constrains the values of the potential energy surface parameters which appear in the phase-space theory to such limited ranges of probable uncertainty, that the comparison of our predictions of the rate coefficients with the experimental measurements must be regarded as a crucial test of the theory.

We shall also present theoretical predictions of the recombination rate coefficients for hydrogen atoms in the presence of the noble gas collision partners He, Ar, and Xe, again using the best estimates of the potential energy surface information. Comparisons with the limited experimental data will also be made.

## II. HYDROGEN MOLECULE AS THIRD BODY

The modified phase-space theory was developed for three-body systems, whereas, reactions (1) actually involve a four-body system. However, we first recognize that even at the high temperatures of shock-tube rate measurements, most of the third-body hydrogen molecules are in their ground vibrational state. In addition, estimates of the H + $H_2(v = 0)$ interaction potential, which we shall discuss below, suggest that the total potential energy is not strongly dependent on the relative orientation of the H atom and the $H_2$ molecule for interatomic separations, $r_{H+H_2}$, greater than about 2 Å. Therefore, to a good approximation, it should be possible to treat the H + $H_2$ $(v = 0)$ potential energy surface as being spherically symmetric and, thereby, reduce the four-body problem to an effective three-body problem for $r_{H+H_2} \gtrsim 2$ Å. Monte-Carlo trajectory calculations based on this model of the H + H + $H_2$ system demonstrate that for typical reactive collisions which lead to recombination, the condition $r_{H+H_2} \gtrsim 2$ Å, is satisfied and that the collision times are many times longer (> 100) than the ground vibrational period of $H_2$. Hence, it appeared reasonable to regard the internal motions of the $H_2$ third bodies as being inconsequential insofar as they would have no effect on the motion of the recombining atoms. We have thus treated the third-body hydrogen molecules as "frozen" particles having a mass of 2 a.u.

Various potential energy surfaces have been proposed for the $H_3$ system, both purely theoretical(17-20) and semi-empirical(21-24) surfaces. In principle one should be able to extract information about the potential parameters for the H + $H_2(v = 0)$ interaction by setting two of the hydrogen atoms at their equilibrium separation, $r_e = 0.74$ Å, and then calculating the potential energy for various positions of the third atom. Margenau(25) has actually carried out a first-order perturbation calculation for both the linear and triangular configurations and obtained a potential energy minimum at $r_{e,H+H_2} \approx 3.17 - 3.55$ Å, having a well depth $U_{H+H_2}/k \approx 23° - 38°K$. Unfortunately, even the more recent calculations are still not accurate enough to provide completely reliable values of the potential parameters required. For example, Shavitt et al.(26) estimated that $r_{e,H+H_2} \approx 3.54$ Å and $U_{H+H_2}/k \approx 13°K$, but pointed out that the well depth was not accurately determined. However, the existence of a minimum does appear to be established; thus we have arbitrarily assumed $r_{e,H+H_2} = 3.4$ Å, since the probable uncertainty of $\pm$ 0.2 Å would have no profound quantitative effect on our results.

Elastic scattering of thermal energy beams is a source of relevant information concerning the potential minimum. In particular, Herschbach and his co-workers(27,28) have deduced from the velocity dependence of total scattering cross sections for H on $H_2$ that $(Ur_e/k)_{H+H_2} \approx 130°K\text{Å}$. Using the previous estimate of $r_{e,H+H_2} \approx 3.4$ Å, we obtain $U_{H+H_2}/k \approx 38°K$.

As in reference (13), we have used the Morse form:

$$V(r) = U\{1 - \exp[-\beta(r - r_e)]\}^2 - U \qquad (2)$$

to describe the H + $H_2$ pair-wise interaction potential where $r_{e,H+H_2} = 3.4$ Å, and $U_{H+H_2}/k = 38°K$. The remaining potential parameter, $\beta_{H+H_2} = 1.48$ Å$^{-1}$, was chosen so that it matched the slope of the repulsive exponential potential which was deduced by Vanderslice and Mason(29) using their semi-empirical "perfect pairing" procedure. The Morse curve given by the above set of potential parameters is shown in Figure 1 together with the Marganau and Vanderslice and Mason portions of the potential.

The effective two-body potential for the H + $H_2$ system, given by Equation 2, and the potential for the ground state $(^1\Sigma_g^+)$ of $H_2$, which was also represented by a Morse form ($U_{H+H}/k = 55200^\circ K$, $r_e = 0.74$ Å, $\beta = 1.92$ $Å^{-1}$) were combined to yield the effective "dumbbell" three-body potential of the H + H + $H_2$ system. The calculation of $k_r^{(H_2)}$ was then carried out in the same manner as described in reference (13).

Figure 2 shows the comparison of our theoretical prediction of $k_r^{(H_2)}$ (full line) with the various experimental data. Although the shock tube results were primarily reported in the form of dissociation rate coefficients, $k_d^{(H_2)}$, we have used the equilibrium constant: $K_e = k_d^{(H_2)}/k_r^{(H_2)}$, to effect a comparison in Figure 2.

Our theoretical values of $k_r^{(H_2)}$ appear to be about 30 per cent lower in absolute magnitude than the recent low temperature recombination rate measurements of Ham, Trainor, and Kaufman(5) although, as can be seen from the inset in Figure 2, the theory reproduces the temperature dependence remarkably well. At high temperatures the prediction is well within the experimental bounds set by Hurle, Jones, and Rosenfeld(12) and is about 50 per cent lower than the results of Jacobs, Giedt, and Cohen,(11) and Sutton.(10) Again, the theory appears to duplicate the temperature dependence of all the measurements to within the probable experimental uncertainties.

In Figure 2 we also show the recent quantum mechanical "resonance theory" prediction of $k_r^{(H_2)}$ by Roberts, Bernstein, and Curtiss.(30) This theory assumes recombination to occur via the "energy transfer" mechanism; i.e.,

$$H + H \rightleftharpoons H_2^i \tag{3a}$$

$$H_2^i + M \rightarrow H_2^n + M \tag{3b}$$

where the $H_2^i$ are relatively long lived "orbiting resonances" having energies greater than the dissociation energy but which are imbedded in the continuum by the rotational barrier. The orbiting resonances are assumed to be formed by quantum mechanical tunneling through the rotational barrier. By identifying certain important resonant states, the collisional de-excitation of which represents the rate-limiting step for recombination to the truly bound states $H_2^n$, Roberts, Bernstein, and Curtiss were able to compute the net recombination rate coefficient in terms of the de-excitation cross sections of the resonant states; these were calculated using approximate quantum mechanical methods.

Although the phase-space theory is purely classical, it too embodies the energy transfer mechanism, but because we assume that the H + $H_2$ interaction potential has an attractive minimum, it also takes account of the additional "chaperone mechanism"; i.e.,

$$H + H_2 \rightleftharpoons H{\cdot}H_2 \tag{4a}$$

$$H + H{\cdot}H_2 \rightarrow 2H_2 \tag{4b}$$

which may dominate the recombination process at low temperatures. The separate contributions of the "energy transfer" and "chaperone" mechanisms can only properly be determined by statistical sampling of trajectory calculations. However, in order to demonstrate their relative importance, we have computed $k_r^{(H_2)}$ using the interaction potential

$$V(r_{H+H_2}) = U_{H+H_2} \{1 - \exp[- \beta_{H+H_2}(r - r_e)\}^2 \; ; \; r_{H+H_2} < r_{e,H+H_2}$$

$$V(r_{H+H_2}) = 0 \; ; \; r_{H+H_2} > r_{e,H+H_2} \qquad (5)$$

By so doing, we have eliminated the attractive potential well but have retained the repulsive part of the previous Morse potential intact. The result of this calculation is shown by the dashed curve in Figure 2. The difference between this and the previous calculation is not entirely due to the chaperone mechanism since, with a Morse potential, energy transfer can take place both during the repulsive and attractive phases of the collisions. However, it is apparent that the attractive minimum in the interaction potential is an important consideration at low temperatures. Our calculation of $k_r^{(H_2)}$, which assumes the purely repulsive interaction, shows no evidence of a maximum at $100^\circ$K as does the resonance theory of Roberts, Bernstein, and Curtiss.$^{(13)}$

We have pointed out previously that the major temperature dependence of the low temperature recombination rate is determined by the factors $\exp(U_{H+H_2}/kT)$ which appear explicitly in the expression for the "barrier rate coefficient" (see Equation 2.10, reference 13). Thus careful measurements of the temperature dependence of the recombination rate coefficient at low temperatures should provide an estimate of the well depth $U_{H+H_2}$.

Although, as we have mentioned above, our theoretical prediction of $k_r^{(H_2)}$ does yield the experimentally determined temperature dependence, the results of Ham, Trainor, and Kaufman do not quite extend into the very low temperature region, i.e., $kT \approx U_{H+H_2}$, where we anticipate a linear dependence of log $k_r^{(H_2)}$ on $T^{-1}$. However, their observed temperature dependence clearly supports our assumed value for the well depth.

For the given interaction potential which we have used here, the major uncertainty in the calculation of $k_r^{H_2}$ probably stems from our estimate of the "recrossing correction factor" $(N/N_o)$, and the "non-equilibrium correction factors" $(k/k_e)$, as defined in reference 13. The value $(N/N_o) = 0.4$ was calculated using Keck's(31) semi-empirical correlation formula which was deduced on a statistical basis from the results of trajectory calculations. Little or no temperature dependence of $(N/N_o)$ was observed, but we should point out that these trajectory calculations were carried out for systems in which the iteration potential, $V_{H+M}$, was assumed to be exponentially repulsive. Preliminary trajectory calculations for systems which have a shallow attractive minimum in the interaction potential appear to agree with Keck's earlier results for $(N/N_o)$, although error bounds of $\pm$ 0.06 on the value of $(N/N_o)$ are probably realistic in view of our limited statistics.

The nonequilibrium correction factors $(k/k_e)$ were calculated using the classical diffusion model of the coupled vibration-dissociation-recombination process developed by Keck and Carrier.(32) Again, the results of Keck's earlier trajectory calculations were used to develop a semi-empirical expression for the classical transition probabilities near the dissociation limit for a rotating Morse oscillator. Although this procedure is undoubtedly acceptable at high temperatures, where the major interaction between the molecular atoms and the third body takes place over the steeply rising repulsive portion of the interaction potential, it may lead to errors at low temperatures where the effects of the attractive minimum are felt. According to the Kack-Carrier model, the most important interaction potential parameter is the exponential range $L_{H+H_2}$, which determines the "softness" of the collisions. Thus, in an attempt to account for the attractive minimum in the actual potential, we have used a temperature dependent $L_{H+H_2}$ to calculate the nonequilibrium correction factors by matching the magnitude and slope of the Morse potential, $V_{H+H_2}$, at the internuclear separation distances $a_{H+H_2\pm}$ (for definition see reference 13); these separation distances correspond to configurations of the collision complex where the momentum transfer is maximized.

Although, as Keck and Carrier point out, their model makes no explicit reference to molecular rotation, rotational effects are approximately taken into account by using an effective potential to describe the molecule and by measuring the energy coordinate from the top of the rotational barrier. A more exact treatment is possible in which the diffusion equation is generalized to take account of both the diffusion of energy and angular momentum. However, such a treatment must await the results of further trajectory calculations, and it is by no means clear that for homonuclear molecules it would lead to significantly different results from the present "one-dimensional" approach.

In summary, therefore, it would appear from the comparisons shown in Figure 2, that the modified phase-space theory yields values of $k_r^{(H_2)}$

which are in very good agreement with what we believe to be the most accurate experimental measurements and that as a consequence, our assumed form of the three-body interaction potential must be substantially correct.

## III. NOBLE GASES AS THIRD BODIES

The case with argon as the third body has been treated previously.(14) Those calculations were based on potential parameters derived from simple empirical combination rules. Recently, Luise(33) has completed a critical investigation of various combination rules,* and his detailed study appears to provide consistent estimates for the potential parameters $U_{H+M}$ and $r_{e,H+M}$, which are required in our calculations of the rate coefficients. In addition, the beam scattering measurements of Hershbach and his co-workers(27,28) provide upper bounds to the strength parameter $(Ur_e)_{H+M}$ for the various hydrogen atom-noble gas interactions to be considered. In view of this, we feel it opportune to present the results of modified phase-space theory recombination rate calculations for hydrogen diluted in the representative inert gases: He, Ar, and Xe. We do this in anticipation that measurements of these rates could be made over widely varying temperatures in the interesting low temperature ranges. The potential parameters used in the calculations are listed in Table I.

The recombination rate coefficients $k_r^{(Ar)}$ are plotted versus temperature in Figure 3, together with the available experimental data.(1,4,8,10,11,12,34,35) The lower full curve is based on the values of $U_{H+Ar}$ and $r_{e,H+Ar}$ recommended

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*We are grateful to Professor John Ross of M.I.T. for drawing our attention to this reference.

in reference (33), whereas the upper full curve was obtained using the value of $U_{H+Ar}/k = 60.5^{o}K$, derived as an upper bound from the beam scattering experiments.(27,28) The value for $\beta_{H+Ar} = 1.44\ \overset{o}{A}^{-1}$ was obtained using the empirical formula given by Mason and Vanderelice(36) as before.(14) The dashed curve was obtained using the same values of $U_{H+Ar}$ and $r_{e,H+Ar}$ as the upper full curve but with the reduced value of $\beta_{H+Ar} = 1.3\ \overset{o}{A}^{-1}$. It illustrates the effect of varying this parameter; i.e., by lowering $\beta_{H+Ar}$, the collisions are made less impulsive, and thus the net recombination rate is reduced. From the comparison shown in Figure 3, it appears that the upper bound on $U_{H+Ar}$ gives the value of $k_r^{(Ar)}$ in best agreement with the low temperature meaeurements of Larkin and Thrush,(1,4) whereas at high temperatures all three theoretical curves are probably within the relatively small mutual experimental scatter of the shock-tube measurements. As for the case where $M = H_2$, we feel that the agreement between experiment and theory is very good.

The cases with M = He (full curves) and M = Xe (dashed curves) are plotted in Figure 4. Again, the lower curves were calculated using the values of $U_{H+M}$ and $r_{e,H+M}$ recommended by reference (33), and the upper curves were calculated using values of $U_{H+M}$ derived as upper bounds from the beam experiments. The experimental data(6,7,9,37) shown here are too scanty to say that they support the theory in detail, but there is clearly no significant disagreement. It is apparent that careful experiments carried out over wide temperature ranges for the two collision partners He and Xe could provide another important test of the theory, particularly at low temperatures where the probable discrepancies in the potential well depths should result in marked differences in the temperature dependences of $k_r^{(He)}$ and $k_r^{(Xe)}$.

## IV. CONCLUSIONS

The recombination of hydrogen has been regarded for a number of years as the prototype three-body reaction because of the simple chemical structure of hydrogen, but because of its discrete energy level structure, even in the vicinity of the dissociation limit, it was not clear that a classical description of the collision mechanics would be adequate. However, the comparisons presented here between the results of the modified phase-space theory and the experimental measurements suggest that the classical approach is quite satisfactory. It may be that because the phase-space theory, as we have applied it, takes account of both the energy transfer mechanism and the chaperone mechanism, the quantum mechanical effects which give rise to the low temperature maximum in the energy transfer rate, as predicted by Roberts, Bernstein, and Curtiss,(30) are masked by the dominant contribution of the chaperone mechanism to the overall rate. A possible test of this explanation could be provided by the results of rate measurements, similar to those of Ham, Trainor, and Kaufman,(5) but with He as the collision partner, since it is likely that the H+He interaction potential has an even shallower potential well than does the $H+H_2$ system.

As a consequence of the comparisons shown both here and in the previous work,(14) we suggest that the results of carefully conducted rate measurements in thermal systems can be used to deduce interatomic potential information in the low energy regions where molecular beam scattering techniques cannot easily penetrate.

Finally, it is to be noted that it is the characteristic features of the interatomic potentials which primarily determine the magnitude of the rate coefficients and their dependence on temperature. Thus,the relative efficiencies of various third bodies in promoting recombination are unlikely to be correlated solely on the basis of their atomic masses, which has been a common experimental practice.

### TABLE I

### Morse Potential Parameters

| Species | $r_e$ (Å) | U ($^oK$)* | | β ($Å^{-1}$) |
|---|---|---|---|---|
| | | (a) | (b) | |
| $H-H_2$ | 3.4 | | 38 | 1.48 |
| H-He | 3.7 | 6.8 | 39.2 | 1.87 |
| H-Ar | 4.0 | 27.5 | 60.5 | 1.44 |
| H-Xe | 4.4 | 37.7 | 72.4 | 1.27 |

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*(a) values recommended by reference (33)
(b) values deduced from beam data, reference (27,28).

## REFERENCES

1. Larkin, F. S. and Thrush, B. A., Tenth Symposium (Internationel) on Combustion, p. 397, The Combustion Institute, 1965.
2. Hurle, I. R., Eleventh Symposium (International) on Combustion, p. 827, The Combustion Institute, 1967.
3. Kaufman, F., Ann. Rev. Phys. Chem. 20, 45 (1969).
4. Larkin, F. S., Cen. J. Chem. 46, 1005 (1968).
5. Ham, D. O., Treinor, D. W., and Kaufman, F., J. Chem. Phys., 53, 4395 (1970).
6. Bennett, J. E. and Bleckmore, D. R., Thirteenth Symposium (International) on Combustion, The Combustion Institute, 1971 (in press).
7. Gerdiner, W. C., Jr. and Kistiakowsky, G. B., J. Chem. Phys., 35, 1765 (1961).
8. Patch, R. W., J. Chem. Phys., 36, 1919 (1962).
9. Rink, J. P., J. Chem. Phys., 36, 262 (1962).
10. Sutton, E. A., J. Chem. Phys., 36, 2923 (1962).
11. Jacobs, T. A., Giedt, R. R., and Cohen, N., J. Chem. Phys., 47, 54 (1967).
12. Hurle, I. R., Jones, A., and Rosenfeld, J.L.J., Proc. Roy. Soc. (London), A310, 253 (1969).
13. Shui, V. H., Appleton, J. P., and Keck, J. C., J. Chem. Phys., 53, 2547 (1970).
14. Shui, V. H., Appleton, J. P., and Keck, J. C., Thirteenth Symposium (International) on Combustion, The Combustion Institute, 1971 (in press).
15. Keck, J. C., Adv. Chem. Phys., 13, 85 (1967).
    Keck, J. C., J. Chem. Phys., 32, 1035 (1960).

16. Rice, O. K., *Statistical Mechanics, Thermodynamics, and Kinetics*, (W. H. Freeman, 1967).

17. (a) Glasstone, S., Laidler, K. J., and Eyring, H., *Theory of Rate Processes* (McGraw-Hill Book Co., New York, 1941).

    (b) Eyring, H. and Eyring, E. M., *Modern Chemical Kinetics* (Reinhold Publ. Corp., New York, 1963).

18. Trulio, J. G. and Kimball, G. E., J. Chem. Phys. **28**, 493 (1958).

19. Boys, S. F. and Shavitt, I., University of Wisconsin Naval Research Laboratory Tech. Rept. WIS-AF-13 (1959); Shavitt, I., J. Chem. Phys. **31**, 1359 (1959).

20. Conroy, H. and Brunner, B. L., J. Chem. Phys., **47**, 921 (1967).

21. Sato, S., J. Chem. Phys., **23**, 592, 2465 (1955).

22. Porter, R. N. and Karplus, M., J. Chem. Phys., **40**, 1105 (1964).

23. Cashian, J. K. and Herschbach, D. R., J. Chem. Phys., **40**, 2358 (1964).

24. Salomon, M., J. Chem. Phys., **51**, 2406 (1969).

25. Margenau, H., Phys. Rev., **66**, 303 (1944).

26. Shavitt, I., Stevens, R. M., Minn, F. L., and Karplus, M., J. Chem. Phys., **48**, 2700 (1968).

27. Fluendy, M. A. D., Martin, R. M., Muschlitz, E. E., Jr., and Herschbach, D. R., J. Chem. Phys., **46**, 2172 (1967).

28. Stwalley, W. C., Niehaus, A., and Herschbach, D. R., J. Chem. Phys., **51**, 2287 (1969).

29. Vanderslice, J. T. and Mason, E. A., J. Chem. Phys., **33**, 492 (1960).

30. Roberts, R. E., Bernstein, R. B., and Curtiss, C. F., J. Chem. Phys., **50**, 5163 (1969).

31. Keck, J. C., Discussions Faraday Soc., **33**, 173 (1962).

32. Keck, J. C. and Carrier, G. F., J. Chem. Phys., 43, 2284 (1965).

33. Luise, R. R., Ph.D. Thesis, M.I.T. (1970).

34. Myerson, A. L. and Watt, W. S., J. Chem. Phys. 49, 425 (1968).

35. Gay, A. and Pratt, N. H., Private communication.

36. Mason, E. A. and Vanderslice, J. T., J. Chem. Phys., 28, 432 (1958).

37. Halstead, C. J. and Jenkins, D. R., Combustion and Flame, 14, 321 (1970).

# FIGURE CAPTIONS

Figure 1. Interaction potential $V_{H+H_2}$ versus distance $r_{H+H_2}$ between the hydrogen atoms and center of mass of the hydrogen molecule. ———— , Morse potential, Equation 2. - - - - , Margenau(25) and Vanderslice and Mason.(29)

Figure 2. Recombiantion rate coefficients $k_r^{(H_2)}$ versus temparature. ———— $k_r^{(H_2)}$ theoratical assuming Morse potential, Equation 2. - - - - $k_r^{(H_2)}$ theoretical assuming repulsive potential, Equation 5. (RBC) Roberts, Bernstein, and Curtiss(30) resonance theory. ○ , Ham, Trainor, and Kaufman;(5) ●, Bennatt and Blackmore;(6) ▼, Larkin and Thrush(1,4) (G) Gardiner and Kistiakowsky;(7) (P) Patch;(8) (R) Rink;(9) (J) Jacobs, Giedt and Cohan;(11) (S) Sutton;(10) (H) Hurle, Jones and Rosanfeld,(12) (UB) upper bound, (BF) best fit.

Figure 3. Recombination rate coefficients $k_r^{(Ar)}$ versus temperature. ———— , - - - - - $k_r^{(Ar)}$ theoretical, see text and Table I. ○, Larkin;(4) ●, Gay and Pratt;(35) (J) Jacobs, Giedt, and Cohen;(11) (H) Hurle, Jones, and Rosenfeld;(12) (P) Patch;(8) (M) Myerson and Watt;(34) (S) Sutton.(10)

Figure 4. Racombiantion rate coafficients $k_r^{(He)}$ and $k_r^{(Xe)}$ versus temparature. ———— $k_r^{(He)}$, - - - - $k_r^{(Xa)}$ theoretical, see text and Table I. ● , $k_r^{(He)}$ Bennett and Blackmore;(16) □ , $k_r^{(He)}$ Halstead and Jenkins;(37) (G), $k_r^{(Xe)}$ Gardiner and Kistiakowsky;(7) (R), $k_r^{(Xe)}$ Rink.(9)

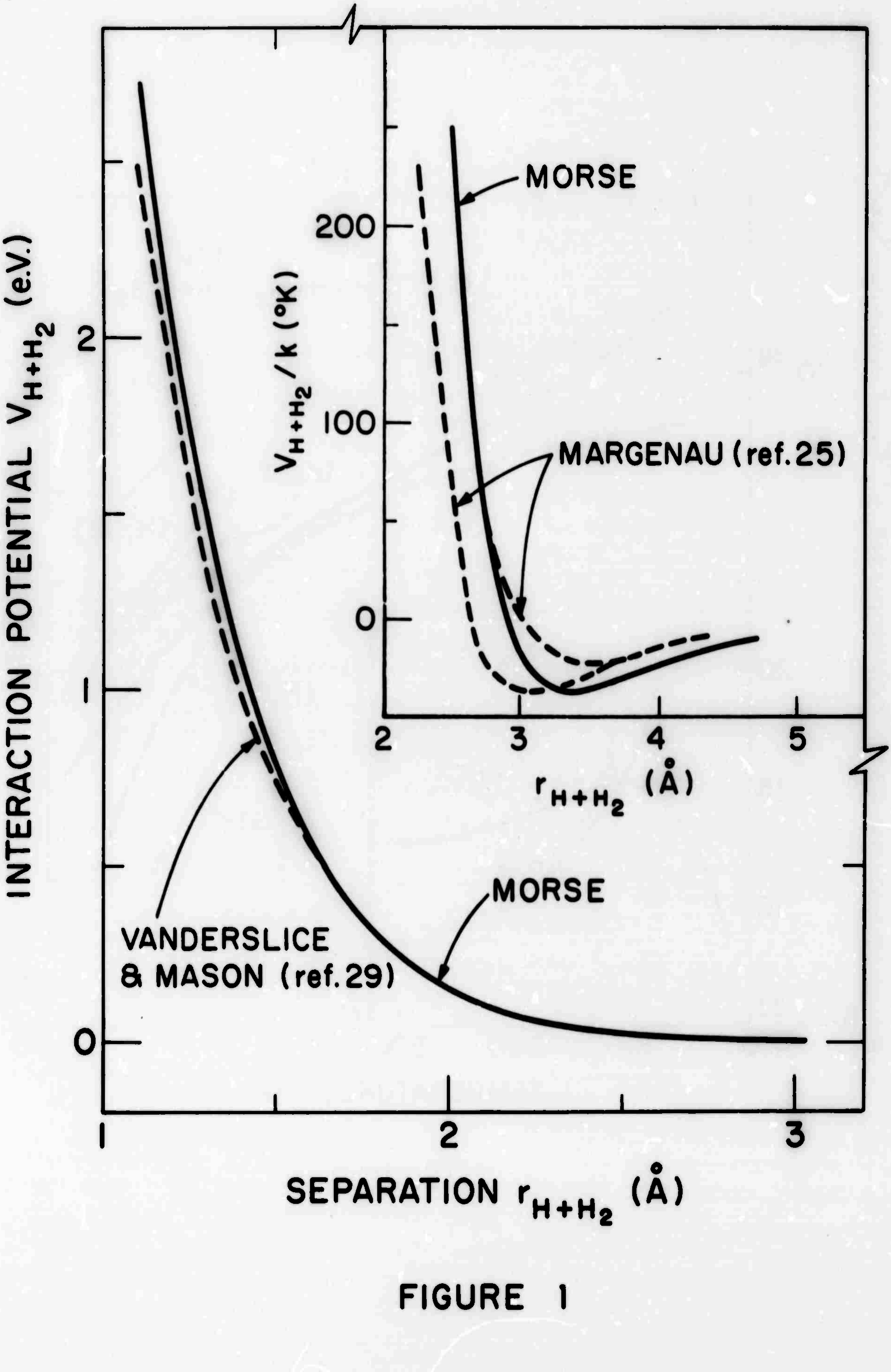

INTERACTION POTENTIAL $V_{H+H_2}$ (e.V.)
0
1
2
1
2
3
SEPARATION $r_{H+H_2}$ (Å)
VANDERSLICE & MASON (ref. 29)
MORSE
$V_{H+H_2}/k$ (°K)
0
100
200
2
3
4
5
$r_{H+H_2}$ (Å)
MORSE
MARGENAU (ref. 25)

FIGURE 1

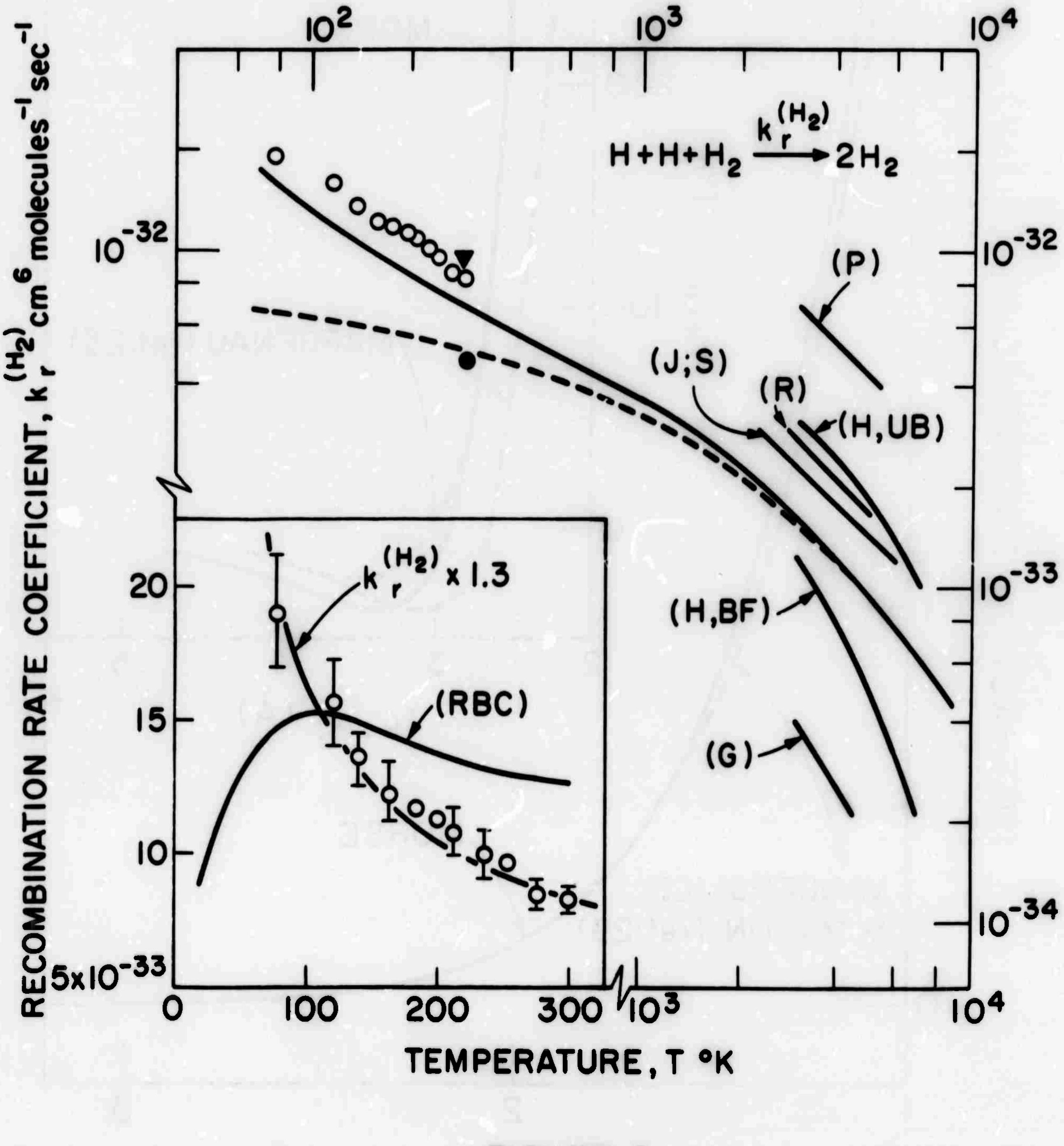
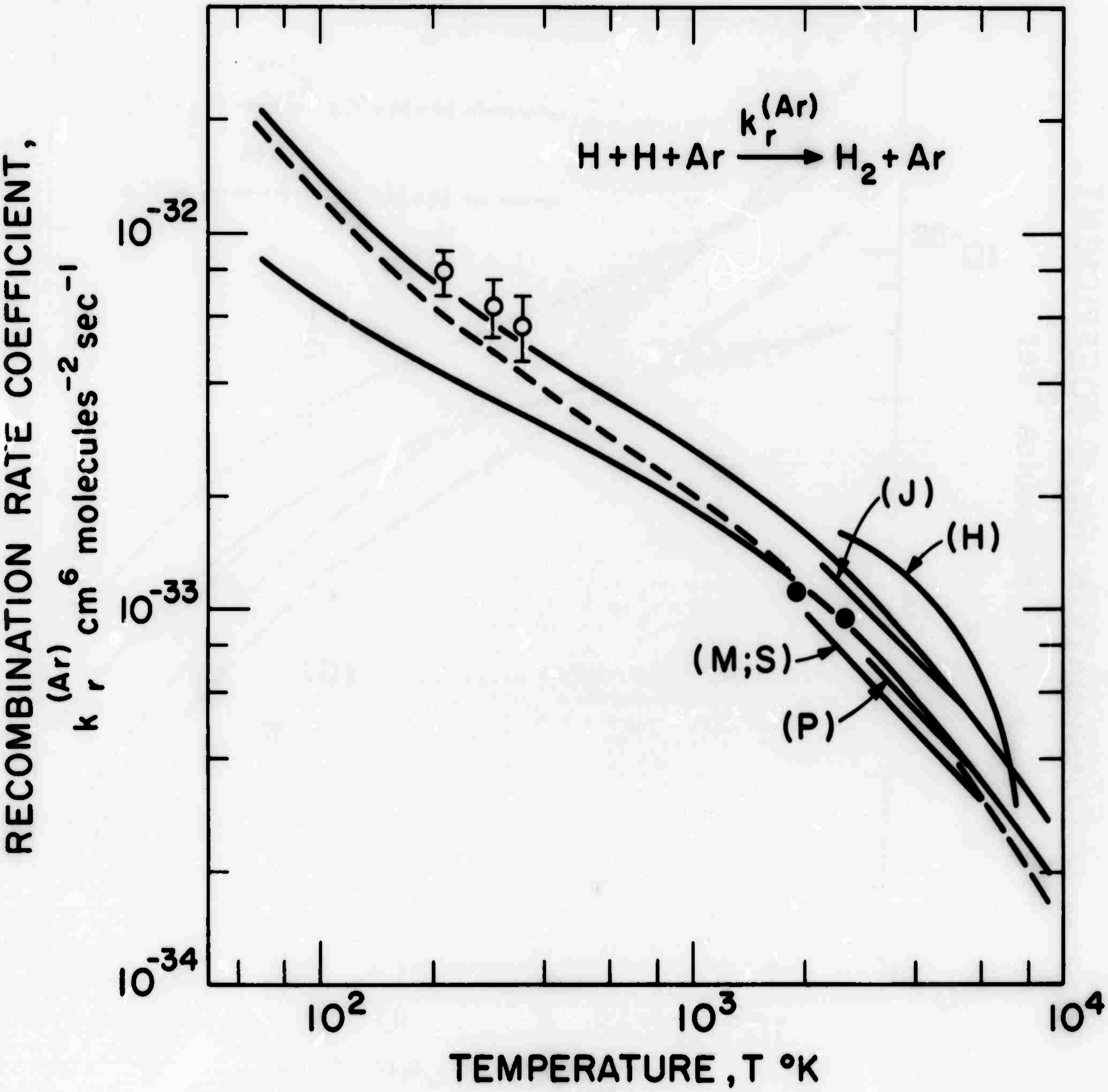

$10^2$
$10^3$
$10^4$
RECOMBINATION RATE COEFFICIENT, $k_r^{(H_2)}$ cm$^6$ molecules$^{-1}$ sec$^{-1}$
$H + H + H_2 \xrightarrow{k_r^{(H_2)}} 2H_2$
$10^{-32}$
$10^{-32}$
(P)
(J;S)
(R)
(H,UB)
$10^{-33}$
(H,BF)
(G)
$10^{-34}$
20
15
10
$5 \times 10^{-33}$
$k_r^{(H_2)} \times 1.3$
(RBC)
0
100
200
300
$10^3$
$10^4$
TEMPERATURE, T °K

FIGURE 2



$H + H + Ar \xrightarrow{k_r^{(Ar)}} H_2 + Ar$
RECOMBINATION RATE COEFFICIENT,
$k_r^{(Ar)}$ cm$^6$ molecules$^{-2}$ sec$^{-1}$
$10^{-32}$
$10^{-33}$
$10^{-34}$
$10^2$
$10^3$
$10^4$
TEMPERATURE, T °K
(J)
(H)
(M;S)
(P)

FIGURE 3

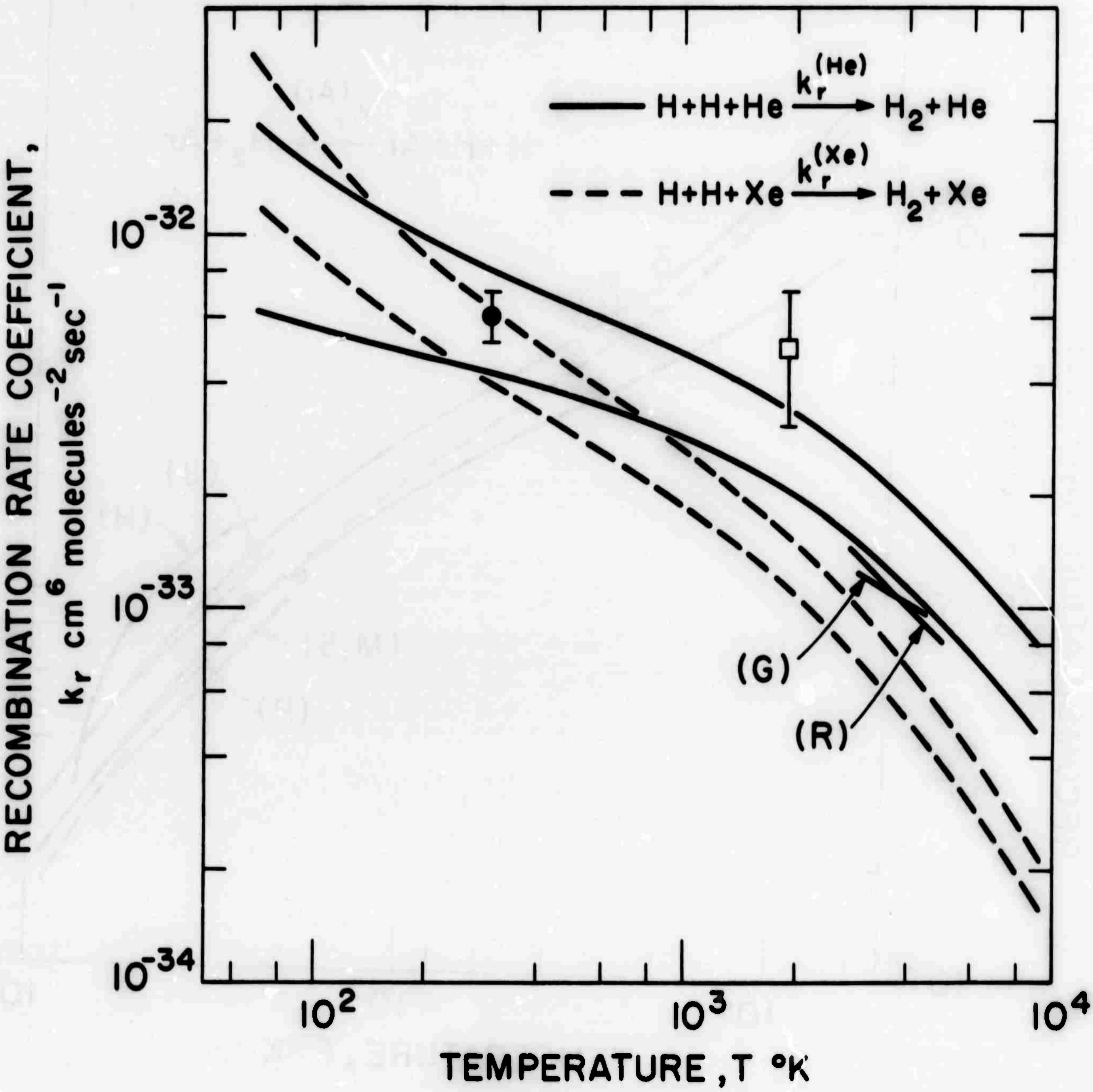

RECOMBINATION RATE COEFFICIENT,
$k_r$ cm$^6$ molecules$^{-2}$sec$^{-1}$
$10^{-32}$
$10^{-33}$
$10^{-34}$
$10^2$
$10^3$
$10^4$
TEMPERATURE, T °K
H+H+He $\xrightarrow{k_r^{(He)}}$ $H_2$+He
H+H+Xe $\xrightarrow{k_r^{(Xe)}}$ $H_2$+Xe
(G)
(R)

FIGURE 4

Unclassified

Security Classification

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*(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)*

**1. ORIGINATING ACTIVITY** *(Corporate author)*

Massachusetts Institute of Technology
Cambridge, Massachusetts

**2a. REPORT SECURITY CLASSIFICATION**

Unclassified

**2b. GROUP**

Fluid Mechanics Laboratory

**3. REPORT TITLE**

Gas Phase Recombination of Hydrogen
A Comparison Between Theory and Experiment

**4. DESCRIPTIVE NOTES** *(Type of report and inclusive dates)*

**5. AUTHOR(S)** *(Last name, first name, initial)*

Shui, Ven H. and Appleton, John P.

**6. REPORT DATE** February, 1971

**7a. TOTAL NO. OF PAGES** 24

**7b. NO. OF REFS** 37

**8a. CONTRACT OR GRANT NO.**

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**c.**

**d.**

**9a. ORIGINATOR'S REPORT NUMBER(S)**

Fluid Mechanics Laboratory
Publication No. 71-4

**9b. OTHER REPORT NO(S)** *(Any other numbers that may be assigned this report)*

**10. AVAILABILITY/LIMITATION NOTICES**

Distribution Unlimited

**11. SUPPLEMENTARY NOTES**

**12. SPONSORING MILITARY ACTIVITY**

Advanced Research Projects Agency of the Department of Defense and monitored by the Office of Naval Research

**13. ABSTRACT**

The modified phase-space theory of reaction rates has been used to calculate the three-body recombination and dissociation rate coefficients of hydrogen in the presence of $H_2$, He, Ar, and Xe collision partners. The theoretical predictions, which rely on semi-empirically derived interatomic potential information, are shown to be in excellent agreement with the measured rate coefficients over wide temperature ranges.

| 14. KEY WORDS | LINK A |  | LINK B |  | LINK C |  |
|---|---|---|---|---|---|---|
|  | ROLE | WT | ROLE | WT | ROLE | WT |
| Hydrogen |  |  |  |  |  |  |
| Dissociation |  |  |  |  |  |  |
| Recombination |  |  |  |  |  |  |
| Chemical Kinetics |  |  |  |  |  |  |
| Reaction Rates |  |  |  |  |  |  |

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