to 24,000 pc/kg (*13*). The amount of radioactivity found in the nut endosperm indicated a preferential retention of radium in some stem tissues during the process of upward transfer to leaves and to its subsequent release at the time of fruit formation. Drobkov (*14*) reported an increase in the intake of uranium by plants during blooming and maturation; he further stated that, while radioelements are distributed throughout the whole plant, they concentrate at the growing points, leaves, and fruit-bearing organs.

T. C. Tso
Crops Research Division,
Agricultural Research Service,
U.S. Department of Agriculture,
Beltsville, Maryland 20705
N. A. Hallden
Health and Safety Laboratory,
U.S. Atomic Energy Commission,
New York
L. T. Alexander
Soil Survey Laboratory,
Soil Conservation Service,
U.S. Department of Agriculture,
Beltsville

References and Notes

1. D. K. Mulvany. *Lancet* **1953-II**, 205 (1953); F. W. Spiers and R. D. Passey, *ibid.*, p. 1259.
2. R. C. Turner and J. M. Radley, *ibid.* **1960-I**, 1197 (1960); E. Marsden and M. A. Collins, *Nature* **198**, 962 (1963).
3. E. P. Radford and V. R. Hunt, *Science* **143**, 247 (1964).
4. Z. S. Altschuler, R. S. Clarke, Jr., E. J. Young, *U.S. Geol. Surv. Profess. Papers* No. 314-D (1958).
5. R. B. Moore, *J. Ind. Eng. Chem.* **6**, 370 (1914).
6. *Report of the United Nations Scientific Committee on the Effects of Atomic Radiation* (New York, 1962).
7. W. Jacobi, *Biophysik* **1**, 175 (1963).
8. R. S. Caldecott and L. A. Snyder, *Radioisotopes in the Biosphere* (Univ. of Minnesota Press, Minneapolis, 1960), pp. 30–36.
9. A. A. Drobkov, *Dokl. Akad. Nauk SSSR* **17**, 229 (1957).
10. J. Stoklasa, *Gartenbauwissensshaft* **1**, 141 (1928).
11. B. K. Brunovskii and K. G. Kunasheva, *Akad. Nauk SSSR Biogeokhim. Lab. Tr.* **3**, 31 (1935).
12. R. S. Russell, *Ann. Rev. Plant Physiol.* **14**, 289 (1963).
13. W. V. Mayneord, R. C. Turner, J. M. Radley, *Nature* **187**, 208 (1960).
14. A. A. Drobkov, *Soviet Agron.* **7** (9), 75 (1949).

15. We thank the following for their assistance: J. Allen, J. M. Carr, J. F. Chaplin, E. Hardy, S. B. Hendricks, C. O. Jensen, R. R. Kincaid, J. D. Miles, M. Meyer, J. M. Moseley, and B. C. Nichols; also John Harley for his interest in this research and discussions of the manuscript.

2 October 1964

■

Vibrational Excitation in Some Four-Center Transition States

Abstract. *The rates of substitution of deuterium for hydrogen in homogeneous gas phase reactions between* D_2 *and* HX (X = *H, Cl,* NH_2*, or HS) were measured at high temperatures by single-pulse shock tube techniques. The magnitudes observed and their dependency on concentration indicate that the rates of exchange are much faster than would be attainable were the deuterium to dissociate and the D atoms to react with HX by atomic displacement to produce H* + *DX. Also, these rates were not limited by methathesis through four-center transition states generated by sufficiently energetic collisions between the principal reactants. The results are compatible with the assumption that the rates are controlled by the populations of* D_2 *in about its 6th vibrational energy level.*

The model system for a methathesis reaction in the gas phase is:

$$H_2 + D_2 \rightarrow 2\,HD$$

Soon after the discovery of deuterium this reaction was studied both in a fixed volume and in hot tube flow reactors (*1*).

Under these conditions it was demonstrated that the reaction involves a dissociation

$$H_2 \leftrightarrows 2\,H$$

which is relatively slow in the gas phase but is assumed to be effectively catalyzed by the walls of the reaction vessel and to reach equilibrium rapidly, and an atomic displacement

$$H + D_2 \rightarrow H \cdots D \cdots D \rightarrow HD + D;$$

$$D + H_2 \rightarrow D \cdots H \cdots H \rightarrow HD + H.$$

This step, which designates a chain process, determines the rate of exchange. The second step is the classic prototype for the linear three-center transition state ($H \cdot\cdot H \cdot\cdot H$), the one for which theorists concerned with absolute reaction rates computed their first potential energy surfaces and estimated on an absolute basis the rate of the overall reaction (*2*). It appears that the four-center exchange mechanism was shunted by the three-center mechanism because of the rapid attainment of the dissociation equilibrium on the walls of the containing vessels. Under those conditions the overall activation energy is about 59 kcal/mole, of which 52 kcal comprises half of the dissociation energy of the hydrogen (required for the first step), and the remaining 7 kcal is the required activation energy for the atomic displacement (second step).

During the past 2 years the single-pulse shock tube (SPST) has been developed into an effective tool for studies of homogeneous gas phase kinetics (*3*). One may thus expose a sample of gas (the species of interest highly diluted with argon, 90 to 99 percent) to a temperature pulse of known intensity and duration (dwell time), under completely homogeneous conditions, such that wall effects are negligible. Indeed, the shock tube walls are at room temperature and therefore cannot be a source of atoms, as is unavoidably the case when the necessary heat influx comes through the walls of the vessel. Several H-D exchange reactions have been studied in this manner (*4*).

However, when we first attempted to analyze the results from the pairs of reactants, ($H_2 + D_2$) and ($HCl + D_2$), we encountered perplexing inconsistencies. The rate constants calculated on the basis of a bimolecular process involving a four-center transition state were scattered to a greater extent than is generally observed for experiments with single-pulse shock tubes (see *5*); the magnitudes for these rate constants were 10 to 100 times larger than the maximum computed from bimolecular collision theory. Finally, the data obtained at high temperatures were not compatible with results obtained by conventional techniques, in view of the lower apparent activation energies deduced from our shock tube runs.

The key to the puzzle was provided by the study of H-D exchange between ($D_2 + NH_3$) and ($D_2 + H_2S$) (*6*). In both cases the rate of production of HD followed the relation:

$$d(HD)/dt = k(Ar)(D_2), \qquad (1)$$

being *zero order* in NH_3 or H_2S. Hence, the step controlling the rate cannot be the bimolecular encounter between the principal reactants. In both cases it

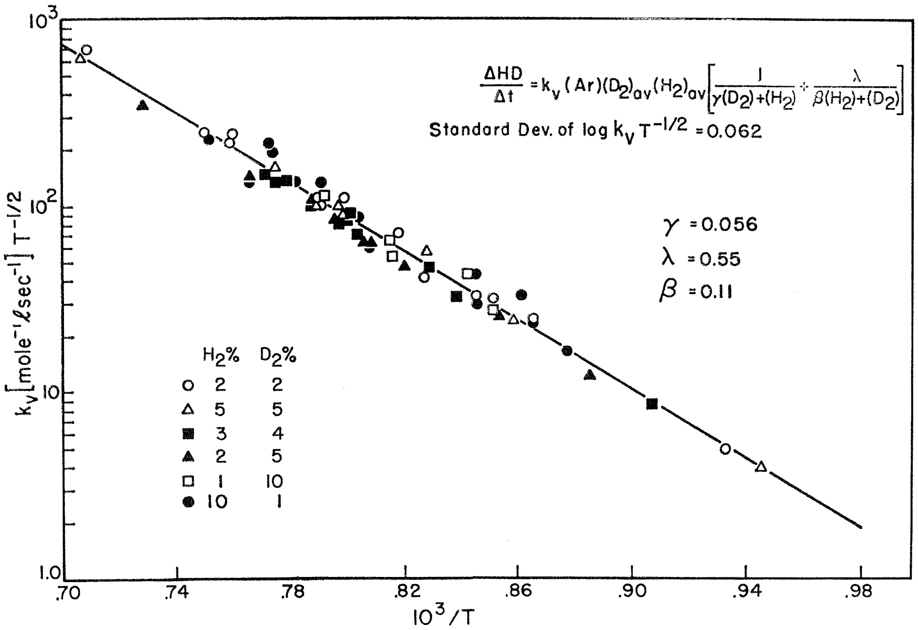

Fig. 1. Graph for activation energy for the homogeneous (H_2 + D_2) reaction (from ref. *11*). The observed exchange rates were reduced to the rate law shown in the upper right hand corner.

must be the activation of the deuterium by collisions with argon. The most plausible mechanism is:

$$D_2 + Ar \underset{k'_\epsilon}{\overset{k'_{-\epsilon}}{\rightleftarrows}} D_2^{(v)} + Ar$$

$$NH_3 + Ar \underset{k_\epsilon}{\overset{k_{-\epsilon}}{\rightleftarrows}} NH_3^{(v)} + Ar,$$

and then

$$D_2^{(v)} + NH_3 \xrightarrow{k'_x} HD + NH_2D$$

$$NH_3^{(v)} + D_2 \xrightarrow{k_x} HD + NH_2D$$

In these equations the k's denote specific reaction rate constants, and the subscripts refer to the corresponding reactions (ϵ, excitation; $-\epsilon$, de-excitation; x, exchange); $D_2^{(v)}$ represents vibrationally excited deuterium. The steady-state condition on $D_2^{(v)}$ and $NH_3^{(v)}$, plus the assumptions that

$$k'_x(NH_3) > k'_{-\epsilon}(Ar)$$

and

$$k_x(NH_3^{(v)})(D_2) \ll k'_x(NH_3)(D_2^{(v)})$$

lead directly to Eq. 1 (*7*). As a matter of interest, two other mechanisms can be postulated which also lead to the observed rate law; however, the assumptions which must be introduced are strained, indeed. The above mechanism implies that in order for hydrogen-deuterium exchange to occur with an appreciable rate, it is necessary for the D_2 molecule to become vibrationally excited to about $v = 6$, and that such a vibrationally excited molecule will react very rapidly with ammonia irrespective of the relative kinetic energy of the colliding pair. The effective rate constant for this excitation is:

$$k'_\epsilon = 10^{11} T^{1/2} e^{(-40,000/RT)} \text{cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}. \quad (2)$$

The net activation energy for the homogeneous exchange reaction as found in our experiments is considerably lower than that expected were the rate-limiting step the formation of a four-centered transition state, for which

$$E \approx 0.28\ [D_{0(H-H)} + D_{0(H-NH_2)}].$$

Before accepting the mechanism proposed above, we demonstrated that the rate is not determined by the homogeneous dissociation of D_2 into atoms followed by a fast reaction with the ammonia:

$$D + NH_3 \rightarrow NH_2D + H$$

with the argon serving as the impact species for the first step. The rate of the homogeneous dissociation of deuterium molecules into atoms has been measured by several investigators (*8*) by shock tube techniques. In the presence of argon, at around 1400°K, the rate constant for dissociation is 8.75×10^{-2} cm^3 mole^{-1} sec^{-1}. On the other hand k'_ϵ, which determines the rate of exchange, is much higher at 1400°K, being approximately 2×10^6 cm^3 mole^{-1} sec^{-1}, or 7.5 orders of magnitude higher. In other words, the number of deuterium atoms generated is very much smaller than the number of NH_2D molecules produced over the same time interval. The presence of a chain as suggested by Farkas (*9*) can also be ruled out:

$$\text{slow:} \quad D + NH_3 \rightarrow NH_2D + H$$

$$\text{fast:} \quad H + D_2 \rightarrow HD + D$$

The extremely long chain which is required to account for the observed rate of exchange should show a dependence on the ammonia concentration, contrary to observation. Furthermore, since the maximum concentration of deuterium atoms which could be present in the reaction mixture is known, one may inquire whether a sufficient number of collisions could occur between these atoms and ammonia during the experimental dwell time to account for the observed HD production. The maximum concentration of atoms which could be present in the reaction mixture is that which may be generated by the homogeneous dissociation process during the 700-μsec dwell time; at 1400°K it is about 10^{-15} mole/cm^3 (much below the equilibrium value). Then

$$\frac{d(NH_2D)}{dt} = k_2(D)_{max}(NH_3) \quad (3)$$

Our data require that $k_2 = 7 \times 10^{16}$ cm^3 mole^{-1} sec^{-1}. Since such an atom displacement reaction would have activation energy of approximately 10 kcal/mole (*2*), k_2 must have a pre-exponential factor greater than 10^{18} cm^3 mole^{-1} sec^{-1}, which is far too high. Finally, the possibility that the H atoms are produced from the decomposition of ammonia is ruled out because of the zero order dependence on the ammonia concentration and the relatively large activation energy ($\approx$ 78 kcal/mole) reported for the pyrolysis of NH_3 (*10*).

We then obtained an additional large set of data on the hydrogen-deuterium exchange reaction, after having considerably improved our shock tube analytical techniques (*11*). Over a range of concentrations of hydrogen to deuterium, from 10/1 through 1/10, the rate of production of HD followed the power rate law

$$\frac{\Delta(HD)}{\Delta t} = k_p (Ar)^{0.98} (D_2)^{0.66} (H_2)^{0.38} \quad (4)$$

where the values for (D_2) and (H_2) are averages. A least squares treatment of these data gave

$$k_p = 10^{(12.60\pm0.41)}T^{1/2}e^{-(42{,}430\pm2290)/RT}\text{cm}^3 \times \text{mole}^{-1}\ \text{sec}^{-1}.$$

The standard deviation of the values of log ($k_p\ T^{-1/2}$) = 0.0907. No theoretical interpretation can be given for this empirical rate law, but it clearly points to the significant role of argon in the activation process. However, if a mechanism similar to that given for the ($NH_3 + D_2$) reaction applies, one would anticipate the possibility of activated deuterium reacting with unexcited hydrogen, and of activated hydrogen reacting with unexcited deuterium, but not with equal probability. This is indicated by the approximate factor of 2 in the power dependence on the concentrations. Thus, for $H_2 + D_2$, where M_i represents the colliding species, $i = 1$ for Ar, $i = 2$ for H_2, and $i = 3$ for D_2.

$$\text{slow:}\quad H_2 + M_i \underset{k_{-\epsilon i}}{\overset{k_{\epsilon i}}{\rightleftarrows}} H_2^{(v)} + M_i$$

$$\text{slow:}\quad D_2 + M_i \underset{k'_{-\epsilon i}}{\overset{k'_{\epsilon i}}{\rightleftarrows}} D_2^{(v)} + M_i$$

$$\text{fast:}\quad H_2^{(v)} + D_2 \underset{k_{-\chi}}{\overset{k_{\chi}}{\rightleftarrows}} 2\,HD$$

$$\text{fast:}\quad D_2^{(v)} + H_2 \underset{k'_{-\chi}}{\overset{k'_{\chi}}{\rightleftarrows}} 2\,HD$$

From these one may derive the expression

$$\frac{d(HD)}{dt} = 2\left[\frac{k'_x(H_2)(D_2)\Sigma(k'_{\epsilon_i}M_i)}{\Sigma(k'_{-\epsilon_i}M_i) + k'_x(H_2)}\right] + 2\left[\frac{k_x(H_2)(D_2)\Sigma(k_{\epsilon_i}M_i)}{\Sigma(k_{-\epsilon_i}M_i) + k_x(D_2)}\right] \qquad (5)$$

In order to reduce this general equation to the one observed, several cases may be considered in detail; the resulting expressions take various forms depending on the ratio $\alpha \equiv (H_2)/(D_2)$. For the range covered in our experiments, to an adequate approximation,

$$\frac{\Delta(HD)}{\Delta t} = k_v(Ar)(D_2)(H_2) \times \left[\frac{1}{\gamma(D_2) + H_2} + \frac{\lambda}{\beta(H_2) + (D_2)}\right] \qquad (6)$$

where

$$k_v = 2\,k_{\epsilon 1}$$

$$\frac{k_{\epsilon 1}}{k'_{\epsilon 1}} = \lambda = 0.55$$

$$\frac{k_{-\epsilon 2}}{k_x} = \beta = 1.1 \times 10^{-1}$$

$$\frac{k'_{-\epsilon 3}}{k'_x} = \gamma = 5.6 \times 10^{-2}$$

$$k_v = 10^{(12.36\pm0.28)}T^{1/2}e^{(42{,}430\pm1570)/RT}\text{cm}^3 \times \text{mole}^{-1}\ \text{sec}^{-1} \qquad (7)$$

The activation energy obtained by plotting the data (Fig. 1) in this manner is 42.43 kcal/mole; it is close to that found for the ($NH_3 + D_2$) reaction. The standard deviation of log ($k_v\ T^{-1/2}$) computed from this equation is 0.0621. The difference by a factor of 20 between the pre-exponential terms in Eq. 7 and Eq. 2 is probably due to insufficient accuracy in the ($NH_3 + D_2$) data. If we assume, as is plausible, that the vibrational activation energy needed for exchange is somewhat higher for ($NH_3 + D_2$) than for ($H_2 + D_2$), the pre-exponential factors could be equal, as is required by the proposed mechanism.

It is interesting to note that our initial data on this reaction, obtained by different experimentors with a different single-pulse technique with much lower concentrations of hydrogen-deuterium (¼ to 2 percent), scatter with about three times the standard deviation around the line given in Fig. 1 (*12*). Although the available rate data on the reaction between ($HCl + D_2$) (*13*) were not obtained with high precision they have been partially analyzed according to the above mechanism. If reduced according to the initial postulate that $d(HD)/dt = k(HCl)(D_2)$, one set of data, obtained in the incident shock region by measuring the intensity of DCl emission in the infrared, gave rate constants which were about three times as large as those similarly evaluated from single-pulse runs. However, the two sets of values are in reasonably good agreement if reduced on the basis of $d(HD)/dt = k(HCl)^{0.6}\ (D_2)^{0.8}\ (Ar)^{0.6}$, but the scatter is larger than desirable. We concluded that the difficulties mentioned in the introduction were due to the naive assumption that the H-D exchange process is rate limited by the formation of a four-center transition state. Our data demonstrate that the exchange process is rate limited by vibrational excitation, and due to the rapidity of the subsequent exchange step nothing can be said about the nature of the transition state, which may indeed consist of a vibrationally excited four-center configuration.

In unimolecular processes, the minimum energy required for the disruption of a bond must first accumulate in the molecular vibrational modes, and eventually get localized in the critical coordinate in order that the reaction may take place. It is assumed that in general bimolecular processes the activation energy may be distributed over all the degrees of freedom of the supermolecule (*14*). However, the mechanism deduced for the foregoing exchange reaction requires that in this type of bimolecular process a much more stringent condition for activation be imposed. There is a low probability for reaction between molecules in their ground or low-lying vibrational states even though their relative kinetic energy along the line of centers exceeds the minimum required (42 kcal/mole). However, the probability for exchange is high, irrespective of their relative kinetic energy, provided the D_2 (or H_2) is excited to its 6th (or 4th) vibrational level. Hard collisions with large amounts of momentum normal to the direction of separation are not particularly effective, whereas large vibrational amplitudes which provide momentum along the direction of separation are effective. This appears to be the first clear example for the requirement of localized excitation in an exchange reaction of the type

$$AB + CD \rightarrow AC + BD$$

It may be that the requirement for localizing excitation in exchange reactions is characteristic only of the hydrogen-deuterium system. Study of the exchange reaction

$$O_2{}^{16,\,16} + O_2{}^{18,\,18} \rightarrow 2\,O^{16}O^{18}$$

and the development of a computational program for estimating the populations of the individual vibrational levels around $v = 6$, to establish the sensitivity of the proposed mechanism to the dependence of the excitation rate constant on the vibrational quantum number, would be useful.

S. H. Bauer
E. L. Resler, Jr.
Department of Chemistry, Cornell University, Ithaca, New York

References and Notes

1. A. Farkas and L. Farkas, *Proc. Roy. Soc. London Ser. A* **152**, 124 (1935); but see also G. Boato, G. Careri, A. Cimino, E. Molinary, G. G. Volpi, *J. Chem. Phys.* **24**, 783 (1956).
2. S. F. Boys and I. Shavitt, University of Wisconsin Naval Research Laboratory Technical Report WIS-AF-13 (1959); I. Shavitt, *J. Chem. Phys.* **31**, 1359 (1959); F. T. Wall and R. N. Porter, *J. Chem. Phys.* **36**, 3256 (1962).
3. S. H. Bauer, *Science* **141**, 867 (1963); A. Lifshitz, S. H. Bauer, E. L. Resler, Jr., *J. Chem. Phys.* **38**, 2056 (1963).
4. Details of these studies are being prepared for publication
5. W. Tsang, *J. Chem. Phys.* **40**, 1171, 1498 (1964).
6. A. Lifshitz, C. Lifshitz, S. H. Bauer, to be published.

7. This mechanism rests on the assumption that the vibrational relaxation time for D_2 is sufficiently rapid to maintain almost the equilibrium population in the v-th vibrational state even though the $(v + 1)$ state is kept well below its equilibrium population by reaction. However, the relaxation time cannot be negligibly small. Only one highly provisional value for the vibrational relaxation time for hydrogen has been given [see A. G. Gaydon and I. R. Hurle, in *Eighth Symposium (International) on Combustion* (Williams and Wilkins, Baltimore, 1962), p. 309; R. C. Millikan and D. R. White, *J. Chem. Phys.* **39**, 3209 (1963)].
8. E. A. Sutton, *J. Chem. Phys.* **36**, 2923 (1962); J. P. Rink, *ibid.*, p. 1398.
9. A. Farkas, *J. Chem. Soc.* **1936**, 26 (1936).
10. T. A. Jacobs, *J. Phys. Chem.* **67**, 665 (1963); H. E. Avery and J. N. Bradley, *Trans. Faraday Soc.* **60**, 857 (1964).
11. E. Ossa and S. H. Bauer, in preparation.
12. W. Tsang, C. S. Wong, S. H. Bauer, in preparation.
13. C. M. Sadowski, K. S. Addecott, S. H. Bauer, in preparation.
14. C. N. Hinshelwood, *Kinetics of Chemical Change* (Oxford University Press, New York, 1940), p. 26.

15. Support from the AFOSR contract AF49(638)-716, NASA grant NsG-116-61, and AEC contract AT(30-1)-3211. The complex equipment used in this study could not have been constructed, nor could the large number of experiments have been performed without this assistance.

5 August 1964 ■

Crustal Uplift Southwest of Montague Island, Alaska

During June and July of 1964 the U.S. Coast and Geodetic Survey ship *Surveyor* completed a network of reconnaissance tracklines including bathymetry in and around Prince William Sound and between Kodiak and Montague islands. Several northwest-southeast transects were run within 16 km (10 miles) of the southwest tip of Montague Island because of the faulting and uplift reported there by the U.S. Geological Survey.

A comparison of this work with a hydrographic survey made in 1927 (*1*) shows that submarine crustal uplift is up to 6 m (20 feet) greater than the maximum uplift of 10 m reported for Cape Cleare, Montague Island (*2*). The nature of the uplift is similar to that mapped on Montague Island by the U.S. Geological Survey—that is, northwesterly tilted blocks between northeast-striking, dip-slip faults. A large area of the sea floor was uplifted in excess of 9 m. Maximum uplift occurred just north of the fault where three areas of uplift exceeding 15 m are shown on the map (Fig. 1).

Vertical and horizontal control for the hydrography of 1927 was very strong. Depths were determined by the Submarine Signal Corporation model 312 sonic fathometer which was checked frequently by up and down lead-line casts. Navigation was controlled by measuring horizontal angles between prominent peaks. The work of 1964 was controlled vertically by the Raytheon model DE 723 recording fathometer, and the navigation was controlled mainly by Loran A and radar. The navigational control during 1927 was stronger than that in 1964, but by lining up two major scarps, which are shown in Fig. 1, the 1964 profiles were matched to the data of 1927.

The submarine extension of Montague Island to the southwest is a sediment-free tabular platform. Lead soundings in 1927, and continuous seismic profiling, bottom photographs, and cores obtained in 1964 showed the area enclosed by the 90-m (50 fathoms) isobath to be bare rock. The flatness of the rock platform makes a perfect fit of the 1927 and 1964 surveys unnecessary. Shifting the 1964 lines parallel to the scarps as much as a kilometer altered the uplift values very little. The sediment-free surface eliminates the possibility of changes in depth due to sediment deposition or seismically-induced consolidation since 1927. Tide-gauge records at nearby Seward have recorded no appreciable secular change in sea-level between 1927 and the earthquake of 27 March 1964. All of the movement is attributable to the earthquake.

Ten fathograms made in 1964 were plotted on the 1927 hydrographic survey sheet, scale 1 : 60,000. Best-fits were made with the two scarps being used for control. No shift exceeding 500 m was needed. Cross sections were then constructed with data obtained during both 1927 and 1964. The difference, crustal uplift, is presented on the contour map (Fig. 1).

The extent of the crustal uplift on 27 March 1964 cannot be traced southwest of the 90-m isobath because of the paucity of 1927 data, extensive sediment accumulation, and the sloping bottom. Another shelf area south of

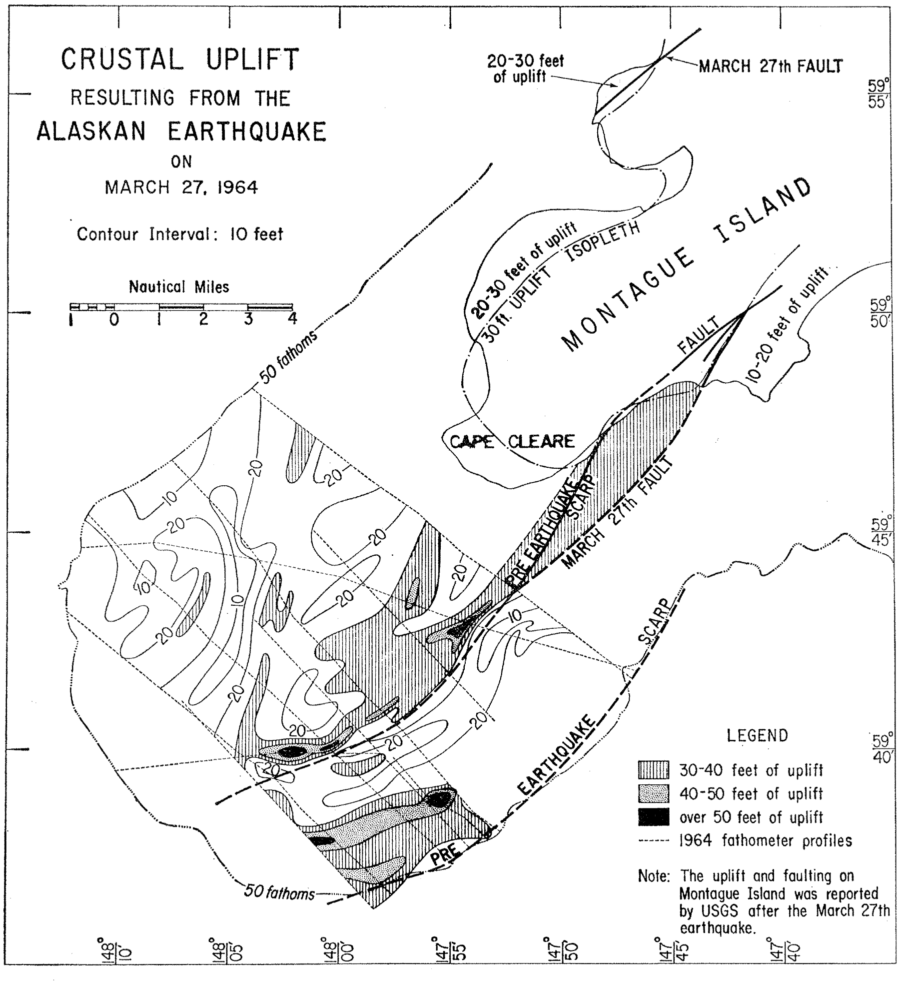

Fig. 1. Contour map of the area between Kodiak and Montague islands. The contour interval, 10 feet, is equivalent to 3 meters. Fifty fathoms are equivalent to 90 meters.