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"Chemical Effects of Nuclear Transformations,
Flash Heating or Flash Photolysis"

Technical Progress Report

February 1, 1967 to October 31, 1967

U.S. Atomic Energy Commission

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Contract No. AT(11-1)-1684
University of Toledo

TECHNICAL PROGRESS REPORT

MASTER

February 1, 1967 through October 31, 1967
Jack G. Kay, Principal Investigator

I. Study of Effects of Flash Heating on
the Surface of an Alumina Catalyst

Mr. W. Ronald Cares has devoted the past year to this problem. Most of his time has been spent in getting the vapor phase chromatograph operating properly and in selecting the type of column for optimum performance. For this, a Perkin-Elmer, Model 820-IV, gas chromatograph and a Sargent, Model SR-25 strip chart recorder were purchased and put to use. Many problems were encountered throughout the summer in getting the chromatograph to operate properly. Many service calls under the manufacturer's warranty were necessary in order to get the correct temperature control and detection efficiency.

The system, presently working satisfactorily, utilizes a heated catalyst pre-column inside the chromatographic oven. Milligram quantities of alumina catalyst work well and, additionally, minimize product absorption. The ethanol samples are injected into the chromatograph, allowed to react on the catalyst and the products, flowing directly through the column, are separated chromatographically.

A reasonable parameter for evaluating the effects of flash heating the alumina prior to use in the catalytic reactor is the activation energy for the reaction of ethanol on the catalyst. The logarithms of the product yields, measured at each reaction temperature, have been plotted against reciprocal temperature to obtain activation energies for the reactions occurring.

DIETHYL ETHER ACTIVATION ENERGY

SAMPLE B

FIGURE 1

DIETHYL ETHER, PEAK AREA UNITS
AT 200°C
SAMPLE B

$$\text{SLOPE} = -4.651 \times 10^3$$

$$E_{\text{ACT}} = 21.27 \pm 0.09 \text{ Kcal/Mole}$$

PEAK AREA ERROR SHOWN BY O
TEMP. ERROR SHOWN BY —

15 Nov 1961
W. E. CHASE

CATALYST SAMPLE B

FIGURE 2

CATALYST SAMPLE B

FIGURE 3

ETHYLENE PEAK HEIGHT
IN 0.02 INCH UNITS

$$\text{SLOPE} = -4.914 \times 10^3$$

$$E_{\text{ACT}} = 22.48 \pm 0.13 \text{ Kcal/mole}$$

PEAK HEIGHT ERROR SHOWN BY $\circ$
TEMP. ERROR SHOWN BY $\pm$ 16 Nov. 1967
W. R. CARB

AVG TEMPERATURE, °K

IN 10^{-3} UNITS

CATALYST SAMPLE B

FIGURE 4

(Water Peak Area at 400°C) - 66
SAMPLE B

$$\text{SLOPE} = -1.433 \times 10^3$$

$$E_{\text{ACT}} = 6.55 \pm 0.02 \text{ Kcal/mole}$$

PEAK AREA STD. DEVIATION, σ , SHOWN BY O
TEMPERATURE⁻¹ ERROR SHOWN BY — —

15 Nov. 1967

W. R. CARES

1.400 1.500 1.600 1.700 1.800 1.900

AVE TEMPERATURE, °K

IN 10⁻³ UNITS

Typical plots for the reaction products, diethyl ether, acetaldehyde, ethylene and water from 12.2 mg. of catalyst for the temperature range 265° - 410° are shown in Figures 1-4. The measured activation energies for production of diethyl ether, ethylene and acetaldehyde in this temperature range are 21.3, 22.5 and 21.8 kcal/mole, respectively. Probably, these values should not be considered as being significantly different from one another at this stage. The activation energy for water production was significantly lower at about 6.6 kcal/mole.

For a 42.2 mg. sample of catalyst, the measured activation energies for diethyl ether and ethylene were 31.9 and 33.5 kcal/mole, respectively, in the range 211° - 369° C. The water showed a more complicated behavior with an activation energy of between 6 and 15 kcal/mole based on an Arrhenius plot of the data.

Literature reports usually discuss only the diethyl ether product in detail and activation energies reported range from 14. to 38. kcal/mole for ether production (1-5)

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1. Balaceanu and Jungers, Bull. Chim. Soc. Belg. 60, 467 (1951)
 2. Bryant and Kranich, J. Cat. 8, 8(1967)
 3. Solomon, Butt and Bliss, I.& E.C. Fund. 6, 325(1967)
 4. Stauffer and Kranich, I.& E.C. Fund. 1, 107(1962)
 5. Kabel and Johanson, A.I. Ch. E.J. 8, 621(1962)
-

The most recent values are 27. kcal/mole (Bryant and Kranich) and 25.4 kcal/mole (Solomon, Butt and Bliss). For ethylene production an activation energy has been reported at 33.kcal/mole (Bryant and Kranich) and at 49. kcal/mole (Solomon, Butt and Bliss).

The literature values, being somewhat higher than our measured values, probably indicate the effect of measuring the build-up of products in a recirculating system rather than in our system which minimizes the accumulation of products on the catalyst. We have observed, for example, distinct differences between the first, second, third and fourth injections on a fresh alumina sample. After the fourth injection, stable catalyst conditions seem to have been achieved. The reasons for this behavior have not been determined.

All measurements thus far have been made on Alumina Catalyst Al-0102 P, Lot 19, furnished by Harshaw Chemical Co. This material has a reported surface area of 140-150 m²/gm and has not yet been treated with a high intensity photoflash. The next step in this work is to measure the activation energies for the catalytic reactions on the same catalyst after exposure to a high intensity photoflash such as used for flash heating in our laboratories. It is anticipated that changes in the alumina due to photoflash exposure with resultant flash heating will create measurable changes in the catalytic surface and that these can be correlated with the catalytic reaction in products, their distribution, and the activation energies for their production.

II. Studies of KMnO_4 Crystals and their Decomposition due to Flash Photolysis and Flash Heating

Mr. Joaquin O. Uy has devoted the past year to this problem. The Ph.D. thesis of Dr. Peter Shu-ti Lee at the University of Illinois serves as the ground work for these investigations. Eventually, it is hoped to understand enough about the flash heating reactions in solids to be able to apply the technique to crystals in which nuclear transformations have occurred so that new information on the hot atom chemical reactions in such crystals may be obtained.

Considerable question exists about the identification of energy levels and the photochemical activity of different wavelengths absorbed by crystalline potassium permanganate. The only spectrum of this crystal in the literature is not of the best quality; therefore, we have measured the absorption spectrum using a Cary-14 Recording Spectrophotometer equipped with a high intensity light source. This spectrum of solid KMnO_4 is shown in Figure 5. The fine structure of the band at $3000\text{\AA}$ is observed in detail. The strong absorption edge occurring at $2000\text{\AA}$ appears like the charge-transfer often attributed to excitation into a conduction band in crystals of the alkali halide type. There appears to be some doubt, however, about whether it is proper to describe crystals such as KMnO_4 in terms of the band theory of solids, and this has been discussed in some detail by Jorgensen.

In order to understand the photochemical effects on such crystals, experiments in thermoluminescence, photoconductivity and photoluminescence have begun with permanganate anions in solids.

The photoluminescence experiments are being carried out in cooperation with Dr. E. C. Lim, Loyola University, and involve the measurement of the luminescence spectrum of permanganate in an alcohol glass at 77°K .

Independent experiments in our laboratory have given evidence that KMnO_4 crystals decompose on exposure to 3100Å light, but no significant decomposition occurs with light in the 5300Å region. Decomposition of aqueous permanganate has previously been shown to occur with a very low quantum yield in the 5000Å region and an increasing quantum yield as the wavelength is decreased.

The apparatus for thermoluminescence has been constructed and utilizes a 1P28 photomultiplier tube to observe the luminescence as the KMnO_4 crystals are warmed up from liquid nitrogen temperature. The photomultiplier output was amplified and displayed on the y-axis of an X-Y recorder. The temperature was indicated along the x-axis by the output of a thermocouple located on the surface of the metal block on which the luminescent crystals were placed. The experiments showed thermoluminescence by KMnO_4 after exposure of the crystals to a low intensity mercury lamp at liquid nitrogen temperature. Control crystals kept in the dark showed no thermoluminescence up to room temperature. Heating rates were determined by simultaneously displaying the thermocouple output on a separate strip chart recorder. The heating rate was not quite constant, but very nearly so and could be controlled manually.

Experiments thus far show that the glow curves obtained are independent of particle size. The shape of the glow curve is dependent upon the rate of heating and the area under the glow curve in each case is proportional to the duration of exposure to the exciting light before warm-up.

Partially thermally decomposed crystals appear to show glow curves similar to those which have been protected from thermal decomposition. In view of the expected photodecomposition due to the shorter wavelength light from the mercury lamp, it appears that thermal and photodecomposition products have the same effect on the glow curves. The area under the glow curve is proportional

to the intensity of light emitted as luminescence as the crystals warm up from -196°C . The luminescence intensity in turn is proportional to the number of electrons excited thermally from trapped states into energy levels from which they can drop into lower states with emission of the observed light. Thus, the number of trapped electrons produced by the exciting mercury lamp is proportional to the duration of exposure to the lamp as would be expected. More evidence must be obtained in order to describe the nature of such traps.

Efforts were made to obtain some idea of the spectral distribution of the emitted light during thermoluminescence. These measurements were made using various filters between the luminescing crystals and the photomultiplier tube. Knowledge of the spectral sensitivity of the 1P28 photomultiplier tube and of the transmission spectrum of each filter allowed general conclusions to be drawn about the emission spectrum. The glow curves are shown in Figures 6-8 and the photomultiplier tube spectral sensitivity in combination with various Corning filters is shown in Figure 9. Examination of these curves leads to the conclusion that relatively little light is emitted with wavelengths shorter than $4000\text{\AA}$ and that most of the observed luminescence is between 4000 and $6000\text{\AA}$. No information was obtainable for thermoluminescence at longer wavelengths because of the spectral response limitations of the PM tube. It is hoped that an alternate PM tube with a different spectral response can be obtained in order to extend these observations to longer wavelengths.

Permanganate crystals exposed to light from a low intensity xenon flash-lamp showed similar glow curves, but with greater intensity.

The depths of electron traps contributing to thermoluminescence were evaluated using Booth's procedure.⁽⁶⁾

6. A. H. Booth, Can. J. Chem. 32, 214(1954).

KMnO_4 crystals:

FIGURE 6

A: 10' irradiation

5×10^{-7} amplifier setting

$y = 0.5 \text{ mV/in}$

$\beta = 0.282^\circ\text{K/sec}$

B: 14' irradiation

5×10^{-7} amplifier setting

$y = 0.5 \text{ mV/in}$

$\beta = 0.68^\circ\text{K/sec}$

Trap depth: $2.4 \times 10^{-3} \text{ e.v.}$

THEROLUMINESCENCE INTENSITY

FIGURE 4

FIGURE 8

FIGURE 4

This method is generally accepted for the first order glow curve peaks(7)

7. P. J. Kelly and M. J. Laubity, Can. J. Phys. 45, 311(1967).

Here, the energy, E, corresponding to the trap depth, was evaluated in terms of the temperatures of maximum glow intensity, T_1 and T_2 , for two glow curves obtained under similar conditions, but using two different sample heating rates, B_1 and B_2 . The relationship is

$$E = k \frac{T_1 T_2}{T_1 T_2} \ln \left[\frac{B_1 (T_2)^2}{B_2 (T_1)^2} \right]$$

k is the Boltzmann's constant.

The trap depths for KMnO_4 are around 2×10^{-3} ev. One experiment with crystals of lithium permanganate suggests trap depths around 3×10^{-3} ev. The explanation for these apparently very shallow traps cannot be given at this time.

A filter transmitting only light of wavelength longer than about $3900\text{\AA}$ was used to filter the mercury lamp used for excitation, also. When this was done, no thermoluminescence was observed, indicating traps contributing to the glow curve were populated by light of wavelength shorter than $3900\text{\AA}$. These observations are consistent with the preliminary results of photoluminescence experiments done at Loyola.

The method of "saw tooth annealing", as suggested by Hill and Schwed(8)

8. J. J. Hill and P. Schwed, J. Chem. Phys. 23, 652(1955).

was employed in an attempt to resolve the glow curve into separate components since a smaller peak was observed in the neighborhood of 0°C in some runs. No resolution was achieved, as indicated in Figure 10.

FIGURE 10

Preliminary conclusions can then be drawn that the traps responsible for thermoluminescence are distributed in energy and are grouped just below the levels into which they may be thermally excited.

A better understanding of these observations might result from consideration of the electronic structure of the permanganate anion. A number of papers appear in the literature on this subject(9-15),

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9. Wolfsberg, M., and L. Helmholtz, J. Chem. Phys., 20, 837(1952).
 10. Ballhausen, C.J. and A.D. Liehr, J. Mol. Spectroscopy, 2, 342 (1958).
 11. Carrington, A. and C.K. Jorgensen, "Relative Molecular Orbital Energies in Tetrahedral Complexes", Mol. Phys. 4, 395 (1961).
 12. Carrington, A. and D.S. Shonland, "The absorption Spectra of Permanganate, Manganate and Related Oxyions", Mol. Phys. 3, 331 (1960).
 13. Fenske, R.F. and C.C. Sweney, "Semi-empirical Molecular Orbital Theory, I. Permanganate and Related Anions", Inorg. Chem., 3, 1105 (1964).
 14. Viste, A., and H.B. Gray, "The Electronic Structure of MnO_4^- " Inorg. Chem., 3, 1113 (1964).
 15. Oleari, L., Gianni de Michelis, and Lorenzo di Sipio, "The Spectra and Electronic Structure of Tetrahedral Ions, I. Chromate and Permanganate Ions", Mol. Phys. 10, 111 (1966).
-

but unfortunately there is considerable disagreement about the proper assignments of various transitions observed in the electronic spectra. The detailed analysis by Oleari, De Michelis, and Di Sipio, published in 1966, appears most reliable at this time and these assignments will be used in evaluating our own results. Substantially, two electronic transitions are assigned to each of the observed absorption bands. The transitions occur from one of the occupied molecular orbitals (t_1 , $2t_2$, $1t_2$) to one or the other of the two lowest empty molecular orbitals ($2e$ and $3t_2$). The transitions are assigned as follows:

From Dr. Lee's thesis and the results of previous workers, it was concluded that photodecomposition of MnO_4^- results in the molecular elimination of oxygen according to the reaction equation

Preliminary results of the photoluminescence experiments suggest that a second product may also be produced, although it has not been detected chemically in any of the previous work. This will require further investigation.

Other experiments which are expected to assist in understanding the photochemical and thermal effects in permanganate crystals involve the study of photoconductivity. An apparatus for photoconductivity measurements is nearly assembled. A high intensity monochromator will be used to select the wavelength of exciting light and the conductivity will be determined utilizing

a vibrating reed electrometer for measuring the extremely low currents. These investigations are expected to give information on the mobility of photo-excited electrons in ionic crystals such as KMnO_4 and to supplement the studies already in progress. It is not expected, for example, that a conduction band would be formed from $3t_2$ levels in the anions of the crystal lattice.⁽¹⁶⁾ On the other hand, mobile electrons have been proposed to react with MnO_4^- , giving $\text{MnO}_4^=$ in flash heated crystals⁽¹⁷⁾.

(16) C. K. Jorgensen, private communication; see also "Orbitals in Atoms and Molecules", Academic Press, 1962, Chapt. 9, and "Halogen Chemistry", Edited by V. Gutmann, Vol.1, Academic Press, 1967, pp.265-401, by Jorgensen.

(17) Peter Shu-ti Lee, Ph.D. Dissertation, University of Illinois, 1966.

III. Flash Heating and Kinetic Spectroscopy Manganese Oxide Problem

Mr. Michael B. Garrett has worked for the past year as an AMU-ANL Fellow in the laboratories of Dr. Frank Tomkins, Argonne National Laboratory. Mr. Garrett has devoted most of his attention to studies of high resolution spectra of MnO . The objective of this work has been to sort out and identify the rotational branches in a prominent band. This should allow the electronic structure to be worked out so as to identify the electronic ground state, which has never conclusively been identified.

At the best reciprocal dispersion of $0.6 \text{ \AA}^{\circ}/\text{mm}$, the rotational lines are unusually broadened and appear to have many perturbations. Attempts to identify the lines in at least one branch have been unsuccessful using the Loomis-Wood treatment on lines considerably distant from the band head. It is possible that the lines are broadened by overlapping, but at the resolution used it appears that this should not be the case. Another explanation for the line broadening might be the hyperfine splitting due to the manganese nucleus, perhaps in combination with the effects of temperature and pressure conditions in the vapor.

Very recently, oxygen-18 enriched potassium permanganate was flash heated and the absorption spectrum of MnO^{18} was obtained. These spectra indicate that some perturbations are removed in the heavy molecule and that a shift of about 20 cm^{-1} towards lower energy occurs in comparison with normal MnO . Bands observed for MnO^{18} are (0,0), and (1,2). The rotational lines are still broadened as with the normal oxide. The (1,2) band edge is observable for the heavy oxide, whereas it was not seen for the lighter molecule. It is expected that these spectra will provide data whereby a better estimate of the vibrational constant may be obtained. This will be used to check the existing value which hasn't been considered very reliable.

IV. Flash Heating and Kinetic Spectroscopy Titanium Monohalides

Mr. Robert L. Diebner working at The University of Toledo has continued his work with titanium monohalides. Little is currently known about transition metal diatomic molecules in spite of the amount of work done in this area. Most experimental spectroscopic work on these compounds involve emission spectra obtained from reactions in electric discharges. Information has also been obtained from high temperature vaporization studies, often using a mass spectrometer for identification and analysis. Such species examined include CrF, MnBr, and many others. In general, bond energy information on this class of compounds is scarce.

The only titanium monohalide for which a spectrum has been reported in the literature is TiCl. All reported TiCl spectra are emission spectra from an electric discharge in TiCl₄ vapor, with the exception of one absorption spectrum produced in shock-heated TiCl₄ vapor(18).

18.W. H. Parkinson and E. M. Reeves (unpublished work)

Our experiments have produced good absorption spectra of TiCl by flash heating either Na₂TiCl₄, TiCl₂ or TiCl₃ (all solids) in argon at reduced pressure.

In some of the TiCl spectra, good spectra of TiO were also obtained, probably as a result of residual oxygen absorbed on the solid prior to flashing. TiO spectra have not yet been obtained by flash heating solid TiO.

Work currently in progress, however, centers on the production and identification of gaseous titanium monofluoride. The optical spectrum of TiF is unknown. Except for the observation of TiF⁺ in the mass spectrum of sublimed TiF₃, there has been produced no definite evidence for the existence of TiF. Thermodynamic estimates indicate that TiF should be the most stable of gaseous titanium monohalides, however.

We have used the TiCl experiments as a guide and have flash heated TiF_3 powder, obtaining absorption band systems that do not correspond to any spectra reported in the literature. These spectra have the general appearance of the TiCl system, but are shifted $100\text{\AA}$ or more to shorter wavelengths. Three sets of bands are observed -- these are in the regions of $3698\text{\AA}$, $3908\text{\AA}$ and $4805\text{\AA}$. The reciprocal dispersion here was $5.4\text{\AA}/\text{mm}$.

The latest experiments have been done with the cooperation of Mr. Garrett and Dr. Tomkins at Argonne using the 30 ft. grating spectrograph (reciprocal dispersion equal to $0.9\text{\AA}/\text{mm}$ in first order). Good spectra were obtained by flash heating TiF_3 in argon and superimposing four experiments on one photographic plate in order to achieve satisfactory darkening. The most intense system ranges from 3984 to $4086\text{\AA}$ and is currently being analyzed. The band separations correspond reasonably well to the expected multiplet splittings of TiF based on observations and published analyses of the TiCl spectra.

As a check on the optical spectroscopy, the Bendix, Model 14-206, Time-of-Flight mass spectrometer at the University of Illinois was used in flash heating experiments with TiF_3 . Runs were made using an ionizing voltage of 20. ev. The principal mass peaks corresponded to TiF^+ species. TiF_3^+ mass peaks were also fairly large. No mass peaks corresponding to TiO^+ were observed, probably because the pressure in the mass spectrometer was low enough to have pumped out any residual oxygen prior to flashing. In the m/e region of Ti^+ , the largest peak was $\frac{m}{e} = 49$. Since the most abundant titanium isotope is mass 48, it appears that a significant amount of TiH^+ was produced. Based on the intensity of the peak at $\frac{m}{e} = 46$, which could not be TiH^+ since Ti^{45} is not naturally occurring, the intensity distribution of the peaks at 47, 48, 49 and 51 are consistent with a relatively higher percentage of TiH^+

being present. TiH^+ has previously been reported being observed in a T.O.F. mass spectrometer from electrically exploding Ti wire in hydrogen(19).

- 19.B. Siegel, International Symposium on High Temperature Chemistry, Argonne, Illinois, May, 1967.
-

The origin of TiH^+ is thought to be from a moisture impurity in the TiF_3 sample.

It should be noted that Ti^{49} has a natural abundance nearly the same as Ti^{50} , yet in the group of mass peaks attributed to TiH^+ , no mass peak was discernable at $\frac{m}{e} = 50$. This has not yet been explained. Time limitations did not allow these details to be explored further on the mass spectrometer, and it may be necessary to schedule time on this instrument at a later date in order to clarify some of these points.

V. Chemical Effects of Nuclear Transformations

Mr. El-Hussieny M. Diefallah has completed his Ph.D. dissertation at the University of Illinois and is starting a postdoctoral appointment in a closely related area at The University of Toledo. The abstract of his dissertation, designated Atomic Energy Commission Report No. C00-1684-1, is copied here.

C00-1684-1

Chemical Effects of Nuclear Transformations and Annealing in Inorganic Crystals

El-Hussieny Mohamed Mohamed Diefallah
University of Illinois-1968
Ph.D. Dissertation Abstract

The chemical effects of radiative neutron capture and associated radiation damage have been investigated for $\text{Os}^{191\text{m}}$ and Os^{193} produced in pure crystals of $\text{K}_4\text{Os}(\text{CN})_6$ and $\text{Ca}_2\text{Os}(\text{CN})_6$, as well as in isomorphous mixed crystals of the type $\text{K}_4\text{Os}(\text{CN})_6 - \text{K}_4\text{Fe}(\text{CN})_6$ and $\text{Ca}_2\text{Os}(\text{CN})_6 - \text{Ca}_2\text{Fe}(\text{CN})_6$. The chemical effects of the isomeric transition $\text{Os}^{191\text{m}}$ (I.T.) Os^{191} were studied in crystals of pure $\text{K}_4\text{Os}(\text{CN})_6$. High voltage paper electrophoresis was utilized for separation and identification of the chemical entities incorporating the hot atom and formed after dissolution of the neutron-irradiated sample in 0.001 N HCl solution. Two osmium chemical states, OsO_2 and the parent $\text{Os}(\text{CN})_6^{4-}$, were observed in this analysis. Individual retentions of $\text{Os}^{191\text{m}}$ and Os^{193} were calculated from the experimental data obtained by assaying the radioactivity associated with the chemical species separated on the paper.

The observed increase in cyanoosmate(II) retention with decreasing mole fraction of the parent in the mixed crystals was found to follow an exponential dependence. This type of dependence is compatible with data reported in the

literature for other types of isomorphous mixed crystals studied. An electron acceptor-donor mechanism involving electron-hole traps and electron recombination centers has been proposed to explain the influence of isomorphous dilution on the probability of parent reformation.

Although isomorphous dilution can cause large changes in parent retention, it does not have much effect on isotope separations. Observed isotopic separations are regarded as due primarily to differences in the charge states established on the two isotopes and to secondary consequences resulting from interactions with the chemical environment. In comparing chemical consequences of (n, γ) and isomeric transition processes, considerations are given to the kinetic energy of the recoil atom, charge states of recoil fragments, and the nature of the chemical environment.

The thermal annealing of osmium nuclear recoils was investigated in crystals of pure cyanosmate(II) and in mixed crystals of the type $K_4Os(CN)_6-K_4Fe(CN)_6$. Isomorphous dilution was found to influence the kinetics and activation energies of the annealing processes. The fast part of the annealing process takes place more rapidly in mixed than in pure cyanosmate(II) crystals. A Fletcher-Brown treatment of annealing data showed that the composite annealing curve in pure and mixed crystals cannot be represented by a single rate process and that a combination of rate processes is more appropriate. Analysis of annealing curves according to the Vand-Primak method gave a spectrum of activation energies ranging from 0.5 to 1.0 eV between room temperature and 192°C, and with an arbitrary frequency factor $B=10^5 \text{ sec}^{-1}$. In mixed crystals the spectrum of activation energies is shifted to lower values. An electron acceptor-donor mechanism involving electron-hole traps and electron recombination centers also seems acceptable for explaining annealing reactions of recoil and radiation damage in pure and mixed crystals and for accounting for the differences observed between the two types of crystals.