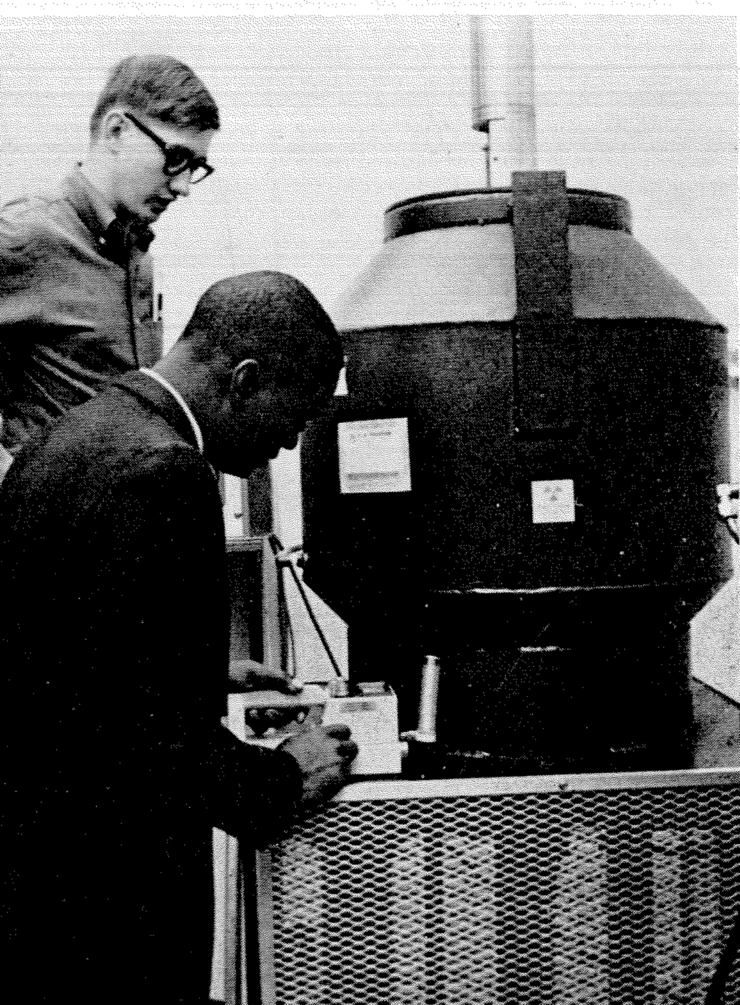
CHEMICAL GAMESMANSHIP



James King Jr., JPL research group supervisor, uses a Geiger counter to check the radaition level around a cobalt-60 gamma ray source. This equipment is used in experiments at JPL done by chemistry graduate student Thomas Penner (upper left).

Caltech scientists are engaged in a kind of scientific gamesmanship in an effort to find out how radiation produces chemical changes in materials.

The research is being done by George S. Hammond, Arthur Amos Noyes Professor of Chemistry and acting chairman of the division of chemistry and chemical engineering, along with other members of his research group. They are taking what is already known about photochemistry—the study of chemical changes produced by light—and applying it to elucidate the fundamental mechanisms of chemical changes initiated by high-energy radiation such as gamma rays.

Gamma rays, which are a very energetic form of x-rays, and light rays are both beams of energy in tiny units called photons. The energy of each gamma photon is much greater than the energies of photons in visible or ultraviolet light. High-energy gamma rays move easily through matter, but when an interaction with a molecule of matter does occur, the molecule literally explodes and ejects high-energy electrons. Most of the chemical changes are not caused directly by these primary interactions but by secondary effects. The electrons produced in the blowup excite other molecules, producing excited states similar to those formed by absorption of light.

The photochemistry of some substances is well known; these substances are used as excitation monitors in the radiochemical experi-

Caltech chemists use what they know about photochemistry to find out more about the fundamental mechanisms of chemical changes initiated by high-energy radiation.

ments. These chemical detectors are put into a system in small amounts, and samples are then irradiated with gamma rays. Excited states of solvent molecules are produced which transfer energy to the test molecules which act as energy scavengers. Analysis is performed to show the extent to which the scavengers have reacted by paths already familiar from photochemical studies. Finally, the results are read backwards to tell the investigator about the forms of excitation deposited along the track of the gamma ray.

Last year John King, now a chemist in the Chevron Research Laboratory in Richmond, California, did work using an organic material called TMO (tetramethyloxetanone) as a scavenger. TMO undergoes an especially simple photochemical reaction in which it falls apart to give two simpler substances, acetone and tetramethylketene. However, decomposition occurs only from excited singlet states of TMO, not from the related triplet excited states. By measuring the yields of the decomposition products from TMO in benzene solutions, Dr. King was able to make the first accurate measurement of the yield of transferable singlet excitations in the gamma radiolysis of benzene.

Sometimes the game turns out to be more complicated than anticipated. At the present time Thomas Penner, a graduate fellow, is studying the gamma-induced reactions of CHD (1,3-cyclohexadiene). The photochemical behavior of CHD has been previously studied carefully by other members of Dr. Hammond's research group, so it seemed easy to use the substance as an energy scavenger. Irradiation of benzene solutions of CHD led to formation of the familiar photoproducts—along with other unexpected products. Apparently the scavenger is catching and using two kinds of excitations. At this stage in their research Dr. Hammond and Mr. Penner believe that the nonphotochemical products arise from positive ions, but still more experiments with scavengers for ions will be required to confirm their suspicions.

Radiation is constantly showered on the earth from the sun, from cosmic rays, and from other natural sources. This radiation bath causes many chemical changes in materials. The consequences range from the life-sustaining storage of light energy by green plants to death from acute radiation sickness in animals.

The Caltech experiments might lead to development of chemical mechanisms for protection against chemical damage from radiation in nonliving materials. In living things, however, the physiological toxicity problems and the dynamic activity within the living system that moves foreign materials around would have to be observed carefully.

The experiments are carried out using the cobalt-60 gamma source at the Jet Propulsion Laboratory and supported by a contract from the Air Force Office of Scientific Research.