

run first in every case but no other minima were found in the region near those recorded which were not observed with the blanks.

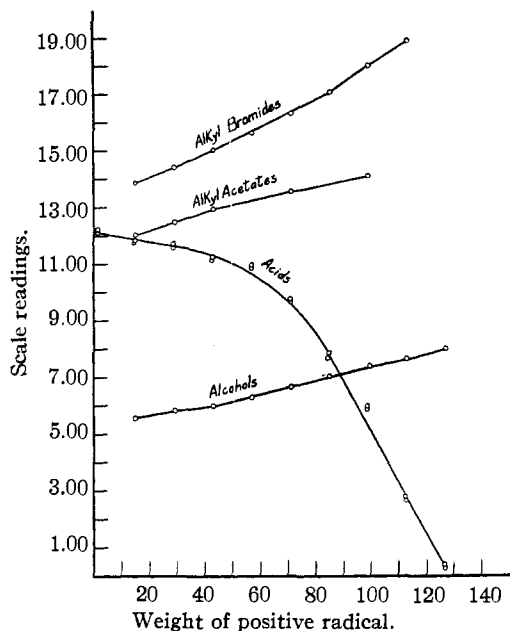


Fig. 1.—Scale readings of various organic compounds on the Allison magneto-optic apparatus.

It will be seen that in each homologous series scale readings for the minima increase with increasing weight of alkyl radical where the radicals are positive, and decrease where they are negative (acids). This is in general agreement with the results of Allison on inorganic compounds [THIS JOURNAL, **52**, 3796 (1930); *J. Chem. Ed.*, **10**, Feb. (1933)].

DEPARTMENT OF BIOCHEMISTRY
EMORY UNIVERSITY
EMORY UNIVERSITY, GA.

J. L. MCGHEE
MARGARET LAWRENZ

RECEIVED MAY 18, 1933 PUBLISHED JUNE 6, 1933

THE TEMPERATURE COEFFICIENT OF THE RECOMBINATION OF HYDROGEN ATOMS

Sir:

A study of the recombination of hydrogen atoms at 25° [I. Amdur with A. L. Robinson, THIS JOURNAL, **55**, 1395 (1933)] indicated that the most probable mechanism for the trimolecular gas reaction is the union of two hydrogen atoms with either a third hydrogen atom or a hydrogen molecule acting as the third body. Assuming no wall reaction the calculated reaction velocity constants showed a definite drift toward lower values at

higher total pressures, disagreeing with the results of Steiner and Wicke [*Z. physik. Chem.*, Bodenstein Band, 817 (1931)], who concluded that the wall reaction is not very significant. Some preliminary measurements have been made at -79 , 0 and 99° by surrounding 20-cm. lengths of the recombination tube with appropriate baths. The results indicate a small but seemingly definite positive temperature coefficient corresponding to an apparent energy of activation of about 900 calories.

There are several reasons for believing that this is further evidence for the existence of a wall reaction. Eyring's [THIS JOURNAL, **53**, 2537 (1931)] potential energy diagram for a three hydrogen atom system is to be interpreted as indicating a zero energy of activation for all possible gaseous trimolecular reactions involving hydrogen atoms and molecules. Reaction rates calculated with the use of kinetic theory diameters for the hydrogen atom and molecule, and assuming no energy of activation, yield reaction velocity constants that are only about half as large as the observed values and although the possibility of resonance interchange [Steiner, *Z. physik. Chem.*, **B15**, 249 (1932)] could increase the effective collision diameters several fold, it seems doubtful that these diameters could be as large as would be demanded by the introduction of the activation factor $e^{-900/RT}$

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA

A. L. ROBINSON
I. AMDUR*

RECEIVED MAY 22, 1933

PUBLISHED JUNE 6, 1933

* At present National Research Fellow in Chemistry at the Massachusetts Institute of Technology.

SEPARATION OF THE ISOTOPIC FORMS OF WATER BY FRACTIONAL DISTILLATION

Sir:

With a twenty-foot fractionating column which has been shown to be equivalent to about forty theoretical plates [Henriques and Cornish, *J. Phys. Chem.*, **37**, 397 (1933)], we have produced appreciable changes in the density of water by separation of the isotopes of hydrogen and oxygen. In our first experiment the ordinary isotopic composition was maintained at the bottom of the column. A stationary state was reached in two days, the water at the top showing a density diminished by 60 parts per million. In our second experiment the ordinary isotopic composition was maintained at the top of the column and samples were taken daily from the bottom. Conditions here were less satisfactory, owing to irregular flow. The density of the samples varied between 70 and 80 parts per million above ordinary water.

Even according to the first estimate [Lewis and Macdonald, *J. Chem. Phys.*, June (1933)] of the concentration of H^2 in ordinary water, which we now believe to be altogether too high, the loss of all the H^2 in the first experiment would cause a diminution in density of only 17 parts