the actual number of molecules reacting, we can calculate the value of the critical increment E. Thus, if k is the velocity coefficient of a bimolecular reaction measured in gram molecules per minute per litre, we have

$$2\sqrt{2}\pi\sigma^2\bar{u}n^2e^{-E/RT}=k\,.\,C^2\,.\,\frac{6\cdot06\,.\,10^{23}}{10^3\,.\,60},$$

where C is the concentration of the reacting substance in gram molecules per litre.

An independent means of determining E is provided by a determination of the temperature coefficient, η, of the reaction and calculating according to the Arrhenius equation

$$\eta=e^{-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T+10}\right)}.$$

So far, the data for three different bimolecular reactions have been available for testing this theory of kinetic activation, namely, the homogeneous bimolecular decompositions of $2N_2O$, 2HI, and $2Cl_2O$, and the two methods of calculating the critical increment give values in good agreement. In the course of an examination of the data of Bodenstein and his co-workers on the formation and decomposition of the higher oxides of nitrogen (*Zeit. Phys. Chem.*, **100,** 68; 1922), I was struck by the fact that his investigation of the thermal decomposition of nitrogen peroxide provides the means of applying yet a further test to the above theory. Bodenstein and Ramstetter (loc. cit.) found that the thermal change

$$2NO_2=2NO+O_2$$

is a homogeneous bimolecular reaction and determined its velocity coefficient at a series of five temperatures between 592° and 656° Abs. From the data given for the velocity coefficient (for example, 204 gram-molecule of $[2NO_2]$ per litre per minute at 627° Abs.) and from the temperature coefficient (1·51 for 10° rise of temperature), the critical increment can be calculated by the two methods outlined above. The only uncertain quantity is the molecular diameter. For this I take the value of $3\cdot33\times10^{-8}$ cm., by comparison with the identical values found by Rankine for the N_2O and CO_2 molecules. In any case the variation in the value of σ makes very little difference to the value of E, which, for example, is only altered to the extent of 3 per cent by a 100 per cent increase in the molecular diameter.

The results of the calculations for nitrogen peroxide have been added to the table of Hinshelwood given below, and the satisfactory agreement will be seen to provide a further confirmation of the theory of kinetic activation.

Reaction. Thermal Decomposition of	E vel. coeff.	E temp. coeff.	Abs. Temp. of Identical Vel. Coeff. (0·0914 g. mol./litre/sec.).
$2N_2O$	55,000	58,500	956
2HI	43,900	44,000	760
$2NO_2$	33,200	32,000	575
$2Cl_2O$	22,000	21,000	384

R. G. W. NORRISH.
Department of Physical Chemistry,
Cambridge University.

Determination of Noon by Shadow.

CORRECT time is now so widely distributed that devices for the accurate reading of sundials are scarcely more than curiosities; but as a curiosity it may be worth while to put on record a method which I used from 1875 to 1880, by which the meridian passage of the sun was determined to within one second by means of a shadow, without any lens or other optical appliance, thus:

A straight rod, R (Fig. 1), in the plane of the meridian was used as the gnomon, and in the same plane and parallel to R was a straight piece of wire, W, at such a distance from R that the diameter of the latter when viewed from W was half the angular diameter of the sun. When the sun is on the meridian, W casts two shadows of equal intensity corresponding to the equal areas of the sun's disc which are not covered by R. The intensity of these shadows changes rapidly with the sun's motion. If R cuts the sun's limb at the four points A, B, C, D, the areas of the sun's disc left uncovered by R are (if $\angle\ AOB=\phi_1$ and $\angle\ COD=\phi_2$) proportional to $\frac{1}{2}\sin\phi_1$ and $\frac{1}{2}\sin\phi_2$, and the ratio of these two quantities gives the relative intensity of the shadow. This is shown in Fig. 2, where the ordinates give the intensity, and the abscissa time in seconds, the unit intensity being that due to illumination by half the sun's disc.

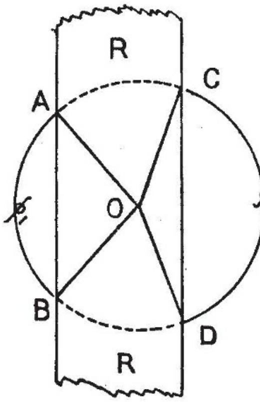

FIG. 1.

It will be seen that when the intensities of the two shadows are identical, the variation in intensity is rather more than 5 per cent per second, a difference which is readily appreciated by the eye, if the screen on which the shadows fall is protected from stray light.

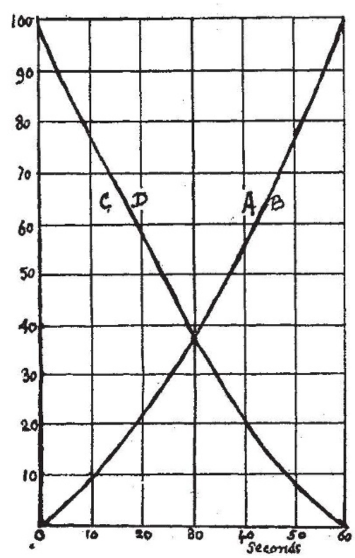

FIG. 2.—Viewed from W, one minute will elapse between the times at which the edge of R is a tangent to the sun's limb, and when the same edge forms a diameter. The curve AB gives the intensity of the shadow of W thrown by that part of the sun exposed between R and AB, CD being the simultaneous intensity of the shadow thrown by the corresponding area between CD and the other edge of R.

A. MALLOCK.
9 Baring Crescent,
Exeter.