In any case, it does not seem reasonable to express the temperature dependence of second-order reactions by a single constant energy of activation or to regard the agreement between the rate of reaction and the product of the collision number with a simple exponential containing an average value for the energy of activation as having any deep theoretical significance. The empirical knowledge that this agreement usually exists, within a factor of ten or so, will of course remain useful.

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[1] See, for example, Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems*, Oxford University Press, **1929**, p. 51.

[2] Rice and Ramsperger, *J. Amer. Chem. Soc.*, **49**, 1617 (1927); Kassel, *J. Phys. Chem.*, **32**, 225 (1928); also various later papers by these same authors.

[3] Bodenstein, *Z. physik. Chem.*, **29**, 295 (1899).

[4] Hinshelwood and Burk, *Proc. Roy. Soc.*, **106A**, 284 (1924).

[5] It is probable that only that component of the relative velocity which is parallel to the line of centers is available, and the distribution law for the kinetic energy resident in this component is the same as for the energy in two squared terms.

[6] The collision rate α is itself proportional to $T^{1/2}$.

ON THE PREDICTIONS OF TRANS-NEPTUNIAN PLANETS FROM THE PERTURBATIONS OF URANUS

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Read before the Academy, April 29, 1930

1. It has always been difficult to understand why predictions of an exterior planet by Lowell and his predecessors, Gaillot, Lau and W. H. Pickering, were possible from the very small residuals which the longitude of Uranus exhibits. The definiteness of these predictions appeared to be quite outside the possibilities of the material under discussion and yet it was not easy to point out any fundamental error in the arguments. The discovery, at the Lowell Observatory, of a new planet in the region predicted suggested a fresh examination of Lowell's work.

The oscillations in the residuals during the interval which has elapsed since the observations were fairly continuous, seem to have periods too short for an explanation on the basis of the existence of an exterior planet, and neither of the two hypothetical planets of Lowell seem to account for them; in any case, their amplitudes are very small. It therefore occurred to me to make an analysis of the following problem. *What are the elements of a planet of given mass and between given limits of distance which will produce small APPARENT perturbations on another planet during a given interval of time, with much larger apparent perturbations* *outside that interval?* The perturbations are *apparent* only because we correct the elements of the known planet so as to assist in making the residuals as small as possible during the interval.

When the two planets move in the same plane, we have eight unknowns at our disposal, namely, the four elements of the hypothetical planet and corrections to the four elements of the known planet. In the case of Uranus an accidental circumstance gives an approximate solution very easily, namely, the fact that the interval which is used is near the synodic period of the two planets. We see at once that there must be approximate symmetry about the middle of the interval. The general trend of the argument is shown by the following example: To determine the values of b, c which will give the least amplitude to the oscillations of

$$\sin t - bt + c$$

between $t = \pm\pi$. The solution gives $c = 0$, $b = 0.23$ and a maximum amplitude of 0.7.

This accidental circumstance gives at once a fictitious longitude at epoch and longitude of perihelion which are almost exactly those of Lowell's hypothetical planets, and it may also give an approximation to the distance within the adopted range of values for this element. It then appears that the actual values which he obtains for the distance, mass and eccentricity substantially depend on three groups of observations made before 1783, having large probable errors. Further, the residuals exhibited by Uranus during the twenty years which have elapsed since the last observation utilized by him in the work seem to bear no resemblance to those which either of his solutions requires. Indeed, it is doubtful if a solution which will substantially account for the new residuals is possible.

It is unfortunate that, if my analysis is correct, so much careful and laborious work can lead to no result. However, in so far as it has stimulated a search for an outer planet which has proved successful, one cannot regret its completion and publication. Perhaps there are other planets beyond the orbit of Neptune, with masses similar to that of the earth or smaller, awaiting discovery.

2. The usual treatment of the observations of a planet involves the calculation of an approximate gravitational theory of the planet's motion and the comparison of this theory with the observations. The elements of the theory are then corrected so as to satisfy the observations as closely as possible. In making these corrections, the later observations are given greater weight than the earlier for well-known reasons. Further, the accuracy of the theory diminishes as we get further away from the epoch of the calculations. On both accounts, therefore, the differences between theory and observation are usually greater in the earlier period than in the later, and they may have a systematic character due to deficiencies

or errors in the gravitational theory. We thus expect—and the expectation is usually fulfilled—an earlier interval of time in which the residuals are larger than in the later interval, partly due to defects in the gravitational theory, partly to inaccuracies in the observations and partly to the method of treatment of the observations.

3. Suppose, however, that we ignore these causes and make the hypothesis that the earlier large residuals and the late smaller residuals are due to the action of an unknown planet. Let the interval of time in which the residuals are small be from $t = t_1$ to $t = t_2$. As a first approximation let us assume that both orbits are nearly circular. We have then the problem of finding the position of a planet such that, during the interval $t_2 - t_1$, its effect on the known planet is small, but outside this interval is greater. If the interval is anywhere near the synodic period of the two planets, we must have conjunction or opposition of the two planets near the middle of the interval, because only in this way can we get minimum oscillations of the function

$$t.\Delta n + t_0 + P(n - n'),$$

where Δn is the resulting change in the mean motion n of the disturbed planet and P is a periodic function with period equal to the synodic period $2\pi/(n - n')$. In other words there must be symmetry about the middle of the interval.

4. Let us apply this result to the residuals in the longitude of Uranus. Those given by Gaillot and adopted by Lowell form a fairly continuous series from 1783 to 1910—an interval of 127 years. These residuals are in general sufficiently small and near together in time to enable us to attribute an occasional larger deviation to errors of observation. There is evidence of systematic variation among them, but the amplitudes are small and they can be neglected in a first approximation.

The observations before 1783 are gathered together into three groups which with their probable errors, are as follows:

1710, $+2''.14 \pm 1''.32$; 1753, $+4''.45 \pm 1''.24$; 1769, $+2''.47 \pm 1''.26$.

We do not know to what extent these residuals are due to errors of observation, nor do we know the nature of the curve which joins them if they are real. The two latter are, however, close enough together in time to enable us to say that there is no maximum or minimum between them if they are real. If these three residuals are given the same weight as the others, we are in fact treating them as real.

We thus have a group of small residuals extending continuously over 127 years, and three isolated earlier groups which depart in a marked manner from the later series.

5. With the assumption of the existence of an exterior planet, we have

to add some hypothesis concerning the distance. If we have too small a distance, we get near the orbit of Neptune and large perturbations of that planet would occur. If the distance is too great, the mass needed becomes much larger. In general, the assumption made is indicated to a considerable extent by the ratios existing between the distances of the eight known planets. Lowell adopts a range of 40.5 to 51.25 units for trial, that is, from 2.2 to 2.6 the distance of Uranus which is 19 units, that of Neptune being 30 units; the unit is the mean distance of the earth from the sun. By Kepler's third law, these limits of distance correspond to periods of revolution of 258 and 367 years, and to synodic periods with that of Uranus of 125 and 109 years, respectively.

The synodic periods are all less than the interval of continuous observation and not very different from it. Therefore, in order to keep the perturbations as small as possible within this interval, we must have symmetry with respect to the middle of the range, that is, conjunction or opposition about the year 1847.

The mean longitudes of Lowell's two hypothetical planets are the same as that of Uranus or differ from it by 180° in 1848.

6. Another point with respect to the assumed distances may be mentioned. The longer the synodic period, the easier it is to keep the perturbations small within the interval, that is to say, for this reason we favor the shorter distance. On the other hand, the shorter the distance, the greater the oscillations for a given mass. There may, therefore, be some distance within the assumed range at which the perturbations will be a minimum for a given interval and a given mass: the existence and position of this minimum, if it exists, would have to be determined by calculation: it could evidently be determined by the method of least squares with the assumption of different distances. The calculations of the perturbations given by Lowell indicate that the length of the interval of observation has had some influence in the determination of the distance, but the extent of this influence is not apparent. The chief influence, however, is the limit of magnitude of the oscillations within the interval as compared with that outside.

It is remarked by Lowell that the residuals of Leverrier appear to give the same date of conjunction as those of Gaillot, although they are much larger and of a quite different character. This resemblance is easily explained in the same way owing to the fact that they cover the same interval and are at a minimum about the middle of the interval.

7. The more unknown constants we have in our equations the easier it is to fit the observations to a given curve. Thus a large eccentricity for the hypothetical planet will assist in keeping the perturbations small within the interval. As Uranus has a rather small eccentricity (0.047), we can neglect it at the outset.

By the same principle of symmetry about the middle date of the interval found in § 4 the planet will necessarily be passing through one of its apses at that time, and we should choose aphelion rather than perihelion as giving the smaller perturbations.

Both of Lowell's hypothetical planets are in aphelion within a year of 1850, that is, close to the middle of the interval.

8. A further test is possible. Suppose that the time of conjunction from the middle date is changed. Then to maintain the symmetry, it is evident that the time of passage through the apse must also be varied.

Lowell has calculated the distance of the planet from perihelion at epoch ($\epsilon' - \tilde{\omega}'$) for various values of ϵ', the mean longitude at epoch. An examination of these values shows that the variation of the mean of ϵ' and $\epsilon' - \tilde{\omega}'$ is not more than 5° for a variation of 40° in ϵ'. Thus $\tilde{\omega}'$ can be obtained as soon as we know ϵ'.

Two of the elements of the hypothetical planet and a rough approximation to a third are obtainable from the single assumption that the perturbations are insensible during most of the interval covered by the observations, this interval including all the more accurate data.

It will be shown below that the application of the hypothetical perturbations to the residuals in this interval actually alters them very little, so that the values of the remaining elements, the eccentricity, the final value of the distance and the mass, depend mainly on the three early residuals given in § 4 above. We have still four constants to consider, namely, the small changes in the elements of the orbit of Uranus. Two of these are substantially used in putting a straight line through the residuals from 1783 to 1910. There are then still five constants at our disposal to satisfy the three early residuals and to assist in keeping the perturbations after 1783 small. The conclusion indicated here that such a determination of the elements of a hypothetical planet has almost no weight is supported by the numerical data which follow.

9. Lowell's method, following those of Adams and Leverrier for the discovery of Neptune, is that of the reduction of the squares of the residuals to a minimum. It is carried out in great detail and apparently with high accuracy. (I have tested some of the coefficients of his computed perturbations.) He gives, however, no probable errors to his results, and although the weights to be assigned to the residuals are shown at the outset, the latter are treated as of equal weight in all of the solutions. As the probable errors vary from 1″.3 for the early groups to 0″.13 for the latest, the proper test of the hypothesis should of course be the percentage reduction of the weighted sum of the squares of the residuals due to the application of the hypothesis.

The sum of the squares of the original residuals is about 55, of which the first three contribute about 30. If we neglected these and put a straight line through the remainder, the sum 25 for them would be reduced to 18.5. This last correction merely consists in determining the mean longitude of Uranus without using the three early groups. The minimum in Lowell's adopted orbits is near 14.5, achieved with nine unknowns and 27 equations of condition. These details give some idea of the extent to which the orbits depend on these three early residuals.

I owe to Dr. D. Brouwer a numerical test of these results. He pointed out that the effect of weighting the observations could be easily calculated in the one case ($\epsilon' = 180°$, $a' = 47.5$) where the equations of condition and the normal equations are given. He first showed that if the mass of the hypothetical planet is made zero we get sensible corrections to the elements of Uranus, indicating that Gaillot had weighted the residuals in the determination of his adopted elements. With m', e', $\tilde{\omega}'$, Δu, $\Delta\epsilon$, Δe, $\Delta\tilde{\omega}$ as unknowns, Dr. Brouwer gets the following values for the percentage reduction of the sum of the squares of the residuals in this case:

Unweighted	+0.58
Weighted according to their probable errors	−0.02
Weighted as suggested (but not used) by Lowell	+0.21

On account of the defects of observations before 1836, known from other sources, the weighting should probably have been about half-way between the second and third of these.

Another approximate test is furnished by noting the range of the sum of the squares of the unweighted residuals for different values of ϵ' and at different distances as given by Lowell. It appears that a range of 40° in ϵ' corresponds to a range of 7 or 8 units in this sum. In view of the small percentage reduction caused by a proper system of weighting it can hardly be doubted that the probable error of ϵ' is at least of the order half a right angle about each of the two possible positions, that is, the occurrence of ϵ' in any one of four quadrants is equally probable.

10. From the same material Dr. Brouwer also suggested and carried out a numerical test of the results given in section 3–7 above. He determined the unknowns and the residuals after the substitution of the values of the former. As expected, the resulting smooth curve determined by the unknowns nearly followed a straight line from 1783 to 1903, running accurately through the residuals at 1769 and 1752 (those of 1710, 1910 are not used by Lowell in this solution). The residuals from 1787 to 1903 are scarcely affected except through being measured from an inclined instead of from a horizontal straight line. And finally the small variations of the curve from a straight line during the interval 1783 to 1903 have the predicted symmetry about the middle date.

11. The existence of this symmetry can be used to indicate the course of the perturbations of Uranus by the hypothetical planet for some years

after 1910—the last date used by Lowell—and to compare them with the observed perturbations. As the curve of prediction runs up sharply about 3″ from 1783 back to 1769, it will run *down* in much the same way from 1910 to about 1926 continuing in the same direction after the latter date. The actual new residuals appear to follow the same general trend as those of the previous century; there is no evidence of a sudden drop.

It may be pointed out here that as these later residuals for 20 years follow the same general run as those of the previous 127 years, if they were treated with the others on Lowell's plan, the predicted place of the planet in 1930 would be altered by about 30°, if a solution is possible. But there is doubt as to whether a planet can be found which will give small residuals for as long an interval as 147 years and still satisfy the early residuals.

12. The question may properly be asked as to whether the results due to the selection and treatment of the material obtained above would have affected the discovery of Neptune by Adams and Leverrier. The answer is in the negative because the conditions present in Gaillot's residuals did not occur in the earlier problem.

In the first place, the interval of 64 years from 1781 to 1845 is only a little more than one-third of the synodic period of 167 years, and there are two marked oscillations in this period which cannot be made small by any adjustment of the elements of the planet. Further, the residuals were much larger than could be attributed to observation or theory. As to the weighting, there was little difference at the time between the earlier and later probable errors—in fact, the observations between 1815 and 1835 are perhaps the poorest in the whole interval. The weighting of the material in a problem of this nature is of fundamental importance because the question of the validity of the hypothesis depends almost entirely on the probable error of the unknowns.

13. The information concerning the newly found planet available at this moment is scanty but it appears to be sufficient to prove that it could not have been predicted from its effect on Uranus. On the most favorable assumption as to albedo (0.06) and density (5.6), the mass cannot be much greater than that of the earth or one-seventh of that predicted by Lowell. At the distance of 40 to 43 units the perturbations of such a planet on Uranus are not within the range of detection from the material available. Among the numerous solutions given by him, only those with an eccentricity of at least 0.5 appear to be possible and these will leave the unweighted sum of the squares of the residuals greater than 22. Such a solution, however, puts the planet more than 30° away from the place where it was found. This last statement refers to the perturbations as actually computed; as a matter of fact, the calculations are quite

inadequate with such a high eccentricity. We must therefore regard the fact that it was found near the predicted place as purely accidental.

Note added May 5: **The orbit published by the Lowell Observatory for the newly discovered planet shows definitely that it cannot have any connection with that predicted.**

THE "REACTION-ISOCHORE" EQUATION FOR IONIZATION WITHIN METALS

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Read before the Academy, April 29, 1930

In a recent number of these PROCEEDINGS I called attention to the fact, previously known but sometimes overlooked, that in order to adapt the Boltzmann distribution equation to the relation between n, the number of free electrons, and n_0, the number of atoms in equilibrium therewith, within a metal, it is necessary to introduce a factor which does not appear in the ordinary use of the equation.

I now propose a similar modification for the relation

$$U = kT^2 \frac{d \ln K}{dT}, \tag{1}$$

called by Nernst[1] the equation of the "reaction-isochore."

Nernst uses this equation with respect to gram-atoms or gram-molecules of material, and he has R, the gas-constant for a gram-molecule, in the second member, where I have k, the Boltzmann constant for a single molecule. The U is in my case the amount of energy required to ionize an atom within the metal. It is equivalent to what I habitually call λ' in my formula

$$\lambda' = \lambda_c' + skT, \tag{2}$$

where λ_c' and s are constants or near constants characteristic of the metal. K is the familiar "equilibrium constant" of a reversible reaction—a quantity, that is, which remains constant during an isothermal reaction.

For the reaction which consists in the break-up of an atom into an ion and a free electron this constant is

$$K = \frac{n^2}{n_0}, \tag{3}$$