

Plotting Kinetic Data To Determine Reaction Order and Specific Rate Constant

Abstract. The Pessen method for obtaining from kinetic experiments both order of reaction and rate constant by means of single straight-line graphs has been combined with the concept of unit time to permit handling of data over the range of 0 to 99 percent conversion or reaction.

A quick and easy method for evaluating reaction rate constants from experimental data has been presented by Pessen (1). His method was limited, however, to the lower conversion ranges (≤ 25 percent) for any order reaction except zero or two. This limit no longer exists if the method is modified as we suggest. The modification is only slightly more involved than the original Pessen method, but is still much easier and faster than the trial-and-error methods in widespread use, and it permits evaluation of data up to 99 percent conversion.

The method is used in the following steps:

- 1) Plot your data as t/f vs. t , where

t is the time elapsed and f is the fractional conversion at this time (1).

- 2) Draw the best straight line through the data and get the slope of this line, or draw the best series of straight lines through the data and get their slopes.

- 3) Enter Table 1 at the conversion (or conversion range) of your data and find the slope that most nearly corresponds with yours. The heading at the top of this column will indicate the reaction order. Since zero order will have a constant slope of zero over the entire conversion range and second order will have a constant slope of one over the entire conversion range, these values are merely noted on the table.

- 4) Pick a representative conversion from the experimental data and note the experimental time value. Find the tabulated "time to get this conversion," for the particular reaction order just determined. The ratio (experimental time : time from Table 1) multiplied by the ordinate intercept from Table 2 gives the ordinate intercept for your particular case in "true time" units.

Since zero order and second order

Table 2. Ordinate intercepts for various reaction orders.

Order	Ordinate intercept, tabulated time units
1/2	0.731
1	0.434
3/2	0.231
3	0.0202

reactions give a linear t/f vs. t relationship, merely extrapolate back to the ordinate if your reaction is of one of these orders.

- 5) Use the true time ordinate intercept to estimate k (1). Ordinate intercept equals $1/ka^{n-1}$, where a is the initial concentration of the reactant and n is reaction order.

In preparing Table 1 only the six reaction orders of integer and half-integer steps are considered (2). Fractional orders other than half are not taken into account since by actual usage the six orders noted here have been found by us to be sufficient for heterogeneous catalysis scale up and correlation requirements.

The concept of time used in the table had an arbitrary basis. Taking the six basic kinetic equations (2) and deciding on a time and conversion [for example, in this case unit time was used as the time required to get 90 percent conversion (3)], k for each reaction order is quickly determined. These k 's are then used to calculate conversion at other levels of unit time. This type of calculation gives t/f in unit time dimensions. Then the slope of t/f vs. t was determined over the short conversion ranges tabulated. The t/f values are not shown since these values are not necessary to the use of this method. The graphical presentation of unit time versus conversion for these six reaction orders has been published (3). Here too, the unit time concept was explained. Using the data of Noddings (3) to determine reaction order is probably comparable to our method as far as ease and accuracy are concerned, but our method gives a bonus in that k is also readily found.

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References

1. H. Pessen, *Science* **134**, 676 (1961).
2. K. J. Laidler, *Chemical Kinetics* (McGraw-Hill, New York, 1950), p. 12.
3. C. R. Noddings, *Chem. Process.* **16**, 63 (1953).

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Table 1. Chart for evaluation of reaction rate constants from experimental data which also permits evaluation of data up to 99 percent conversion. Basis, unit time gives .90 conversion; 0 order, constant slope of 0 for all conversions; 2nd order, constant slope of 1 for all conversions.

Fractional conversion	1/2 Order		1 Order		3/2 Order		3 Order	
	Time to get this conversion	Slope	Time to get this conversion	Slope	Time to get this conversion	Slope	Time to get this conversion	Slope
0.01	0.007		0.004		0.002		0.000*	
.05	.037	.255	.022	.495	.012	.745	.001	1.48
.10	.075	.26	.046	.515	.025	.76	.002	1.465
.15	.114	.26	.071	.525	.039	.765	.004	1.445
.20	.154	.28	.097	.535	.055	.775	.006	1.41
.25	.196	.28	.125	.535	.072	.78	.008	1.385
.30	.239	.295	.155	.555	.090	.775	.011	1.36
.35	.283	.30	.187	.57	.111	.805	.014	1.34
.40	.330	.31	.222	.575	.135	.815	.018	1.31
.45	.378	.325	.260	.595	.161	.81	.023	1.285
.50	.428	.335	.301	.605	.192	.82	.030	1.26
.55	.481	.35	.347	.62	.227	.835	.040	1.235
.60	.538	.365	.398	.64	.269	.845	.053	1.21
.65	.597	.385	.456	.66	.319	.855	.072	1.185
.70	.661	.405	.523	.68	.382	.865	.102	1.165
.75	.731	.43	.602	.705	.462	.88	.152	1.135
.80	.808	.46	.699	.735	.572	.895	.242	1.11
.85	.896	.50	.824	.765	.732	.915	.439	1.085
.90	1.00	.55	1.00	.805	1.00	.935	1.00	1.06
.91	1.02	.58	1.05	.83	1.08	.945	1.24	1.045
.92	1.05	.60	1.10	.845	1.17	.95	1.57	1.045
.93	1.08	.62	1.15	.855	1.29	.955	2.05	1.035
.94	1.10	.635	1.22	.865	1.43	.96	2.80	1.03
.95	1.14	.655	1.30	.88	1.61	.965	4.03	1.025
.96	1.17	.68	1.40	.895	1.85	.97	6.30	1.02
.97	1.21	.71	1.52	.91	2.21	.975	11.2	1.015
.98	1.26	.745	1.70	.93	2.81	.98	25.2	1.01
.99	1.32	.795	2.00	.95	4.16	.99	101.0	1.005
1.00	1.46	.91						