



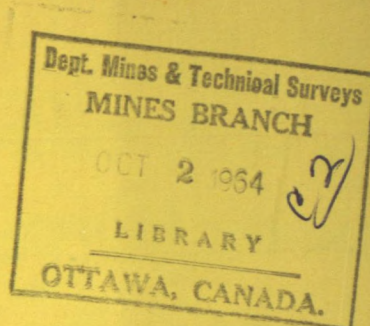
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ACTIVATION ENERGY CALCULATION
FROM A LINEARLY-INCREASING-
TEMPERATURE EXPERIMENT

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EXTRACTION METALLURGY DIVISION

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Activation Energy Calculation from a Linearly-Increasing-Temperature Experiment¹

T. R. INGRAHAM² and P. MARIER³

A simplified method has been developed for the determination of the activation energy of a heterogeneous reaction having linear kinetics.

The thermal decomposition of calcium carbonate has been used as an example and it has been shown that when the logarithm of the weight loss per unit area of powder compacts is plotted against the reciprocal of absolute temperature, for a run done with a linear heating rate, a linear relationship is obtained. When the logarithms of the heating rate and the absolute temperature are included, results for a variety of heating rates can be completely correlated. Heating rates of less than 5 degrees per minute are recommended.

An activation energy of 48.4 ± 2 kilocalories per mole has been estimated for the decomposition reaction and 7 ± 3 kilocalories per mole for the formation reaction.

A recent publication by the authors⁽¹⁾ described studies on the thermal decomposition of calcium carbonate. The activation energy calculated for the decomposition was almost identical with the heat of reaction. This close correspondence of the two energies has been noted previously by Fishbeck and Snaidt⁽²⁾ for a variety of endothermic decompositions. In analysing the possible reasons for this behavior, Garner⁽³⁾ has suggested that the rate-of-decomposition studies were probably conducted under reversible conditions. Both the forward and reverse reactions would be involved, and the magnitude of the change in rate with change in temperature would be controlled by the magnitude of the heat of reaction rather than by either the activation energy of only the forward reaction or of only the reverse reaction.

To determine the activation energy by non-isothermal studies in which equilibrium would be unlikely to obtain, attempts

Une méthode simplifiée a été développée pour la détermination de l'énergie d'activation d'une réaction hétérogène, obéissant à une équation de taux de réaction linéaire.

La décomposition thermique du carbonate de chaux a été utilisée comme exemple et il a été démontré qu'un graphique du logarithme de la perte de masse par unité de surface de poudre en fonction de l'inverse de la température absolue conduit à une ligne droite dans le cas d'un chauffage à taux constant. Il devient alors possible de représenter les résultats expérimentaux correspondants à divers taux de chauffage jusqu'à 5° par minute en introduisant les logarithmes du taux de chauffage et de la température absolue.

L'énergie d'activation de la réaction de décomposition a été estimée égale à 48.4 ± 2 kilocalories par mole tandis que celle de la réaction de formation a été trouvée égale à 7 ± 3 kilocalories par mole.

were made to use the procedures developed by Baur, Bridges and Fassell⁽⁴⁾ and simplified by Kofstad⁽⁵⁾. The method has been reviewed and endorsed for its interesting possibilities by Kubaschewski and Hopkins⁽⁶⁾. The method is based on determining the slope of a weight-change versus temperature relationship at a series of temperatures. This can be a very time consuming and frequently unrewarding task, because the errors in assessing the slopes sometimes approach the magnitude of the change in slope. As a result, erratic relationships may be found, and these may be applicable only over relatively short ranges of temperature and small fractions of the total decomposition⁽⁷⁾.

In this paper, an alternative method of calculating activation energies from linearly-increasing-temperature data will be suggested.

Material, Apparatus and Procedure

The material used in the experiments was reagent-grade, precipitated calcium carbonate which had been compressed at 100,000 p.s.i. to form a disc 0.6476 cm. in diameter and 0.0782 cm. in height. In earlier isothermal experiments by the authors⁽¹⁾,

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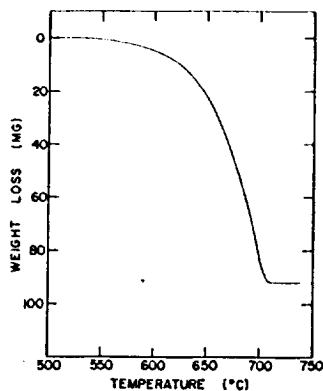


Figure 1—Tracing of: weight loss versus temperature graph drawn by automatic thermogravimetric balance.

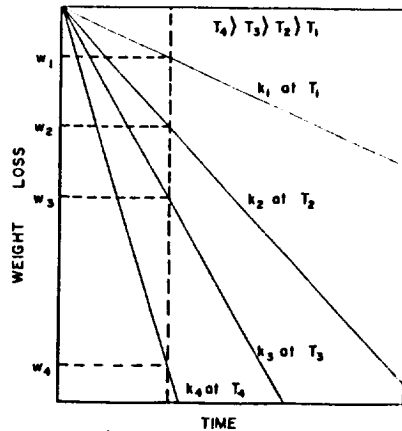


Figure 2—Sketch showing relationship of rate constants to weight losses per unit area, for a constant time interval at a variety of temperatures.

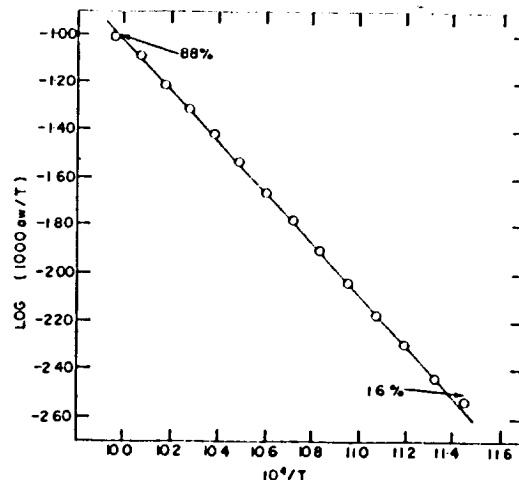


Figure 3—Modified Arrhenius graph for determination of activation energy.

it was established that samples prepared by this technique behaved in the same manner as single crystals of calcite by exhibiting an interface reaction. The rate of inward migration of the interface is constant at a constant temperature, and the observed rate of the reaction at any temperature is a linear function of the area of the interface.

An Aminco] Thermo-grav recording thermobalance was used in the experiments. The balance was fitted with auxiliary gears to permit heating rates of 0.833, 1.64, 2.50 and 5.00 degrees per minute.

In making a run, the calcium carbonate disc was placed on a platinum gauze pan suspended from the balance spring. A preheated stream of dry nitrogen was passed over the pellet at a rate of 50 cu. cm./min. and the pellet was heated at a predetermined linear heating rate. As decomposition occurred, the weight was recorded automatically and plotted as a function of temperature. The weight losses were converted to weight losses per unit interfacial area, using the method previously described by the authors⁽¹⁾.

Analysis of Results

A tracing of one of the weight vs. temperature relationships obtained in these experiments is shown in Figure 1. Because of the large ratio of the diameter to the height of the pellets used, there is only a very small change in the area of the reaction interface as the reaction proceeds from 0-100%. Because of this small change, the relationship is typical of a weight loss per unit area vs. temperature relationship. The similarity in shape of this relationship and a standard pressure vs. temperature relationship for a liquid, suggested the logarithmic method proposed here for the analysis of the results.

According to Laidler⁽²⁾, the logarithm of the specific rate constant, k , is related to the heat of activation, ΔH^\ddagger , and the absolute temperature by the relationship:

$$\ln k = \ln (k/h[e^{\Delta S^\ddagger/R}]) + \ln T - \Delta H^\ddagger/RT.$$

Since the entropy of activation, ΔS^\ddagger , does not usually vary greatly with changes in temperature, the logarithm of the frequency factor, $k/h[e^{\Delta S^\ddagger/R}]$, may be replaced by a constant, $\ln C$. In addition, since it may be presumed that there is no increase in volume on the formation of the activation complex, the heat of activation, ΔH^\ddagger , will be identical with the experimentally determined energy of activation, E .

For a reaction, such as the thermal decomposition of calcium carbonate, which obeys linear kinetics⁽¹⁾, the rate constant may be expressed as $k = dw/dt$, in which dw represents the loss in weight from unit area in a period of time, dt . When the temperature of the sample is increased at a linear rate, the

temperature at any time, t , is $T = b + at$, where a is the rate of heating and b the initial temperature. From this relationship, it is evident that the time interval, dt , is replaceable by dT/a , i.e., $k = adw/dT$, from which it can be shown that;

$$\log (dw/dT) = \log T - \log a + \log C - E/2.303 RT.$$

The activation energy is calculable from the slope of a graph of $[\log (dw/dT) - \log T + \log a]$ vs. $1/T$. The logarithm of the constant term has been eliminated from the equation because it influences only the intercept and not the slope, with which we are concerned. The logarithm of the heating rate, although constant for any particular experiment, is retained in the equation to permit correlation of experiments done at different heating rates. To use this relationship it is only necessary to determine the quantity $\log (a dw/dT)$ from the experimental data.

The method of doing this can be developed most readily by reference to the illustration, of a group of schematic isothermal experiments, in Figure 2. The slopes of the straight lines in Figure 2 are numerically equal to the reaction rate constants: k_1 at a temperature T_1 , k_2 at T_2 etc. It is evident that when the same interval is chosen for comparison of the data, the rate constants k_1 , k_2 , k_3 and k_4 will be directly proportional to w_1 , w_2 , w_3 and w_4 . Because the slope of the weight vs. time

TABLE I
TEMPERATURE AND WEIGHT LOSS DATA FOR VARIOUS
RATES OF HEATING OF CALCIUM CARBONATE DISCS

Temperature °K.	log 1000 aw./T.				Average
	0.833° min. ⁻¹	1.67° min. ⁻¹	2.50° min. ⁻¹	5.00° min. ⁻¹	
873.18	-2.51	-2.61	-2.48		-2.53
883.18	-2.38	-2.48	-2.45		-2.44
893.18	-2.27	-2.33	-2.28		-2.29
903.18	-2.13	-2.22	-2.16		-2.17
913.18	-2.01	-2.09	-2.02		-2.04
923.18	-1.88	-1.95	-1.87	-1.91	-1.90
933.18	-1.76	-1.82	-1.74	-1.78	-1.78
943.18	-1.64	-1.69	-1.62	-1.67	-1.66
953.18	-1.53	-1.57	-1.49	-1.52	-1.53
963.18	-1.37	-1.47	-1.38	-1.42	-1.41
973.18	-1.33	-1.36	-1.27	-1.29	-1.31
983.18	-1.28	-1.24	-1.17	-1.17	-1.22
993.18		-1.13	-1.07	-1.06	-1.09
1003.18		-1.05	-0.99	-0.97	-1.00

curve is the same at a selected value of T , irrespective of whether the temperature is constant or varying at the moment the slope is taken, it is possible to replace $\log(dw/dt)$ directly by $\log w + \text{constant}$. The proportionality constant is included with the frequency factor and is eliminated from the calculation because it does not influence the slope of the relationship, $\log(\sigma w/T)$ vs. $1/T$.

Results

The results of four experiments are shown in Table 1. From these results, calculations were made of the quantity $\log(\sigma w/T)$ for a series of temperatures common to each of the runs, and the graph shown in Figure 3 was prepared from the calculations. Regression analysis has been used to fit the straight line to the points for the region 1.6-88% decomposition. The equation of the regression line is: $\log(\sigma w/T) = 9.556 - 1.058 \times 10^4/T$. The standard deviation is 0.0146. On the assumption that there is a 95% certainty of finding all the results within \pm two standard deviations at the top and bottom of the curve, the energy of activation has been calculated as:

$$E = 48.4 \pm 2.0 \text{ kilocalories per mole.}$$

Discussion and Conclusions

From the data of Kelley and Anderson⁽⁹⁾, the average heat of reaction is 41.2 ± 1.2 kilocalories/mole in the range of

temperature (873-1003°C.) used in these experiments. Acceptance of the experimental value of $E = 48.4 \pm 2.0$ kilocalories/mole as the energy of activation in the forward direction, permits calculation of an energy of activation of 7 ± 3 kilocalories/mole for the reverse reaction. This small activation energy, although subject to a 40% error, is much more reasonable than the zero value suggested by isothermal experiments.

The method of analysis of the data is of greater interest, however, than any individual application such as the one discussed in this paper. There is a substantial possibility that the method may also be applicable to some heterogeneous systems which follow parabolic kinetics.

References

- (1) Ingraham, T. R. and Marlor, P., *Can. J. Chem. Eng.* **41**, 170 (August 1963).
- (2) Fishbeck and Snajdt, *Z. Elektrochem.* **38**, 199 (1932).
- (3) Garner, W. E., "Chemistry of the Solid State" (Butterworths Scientific Publications, London, 1955), pp. 224 and 228.
- (4) Baur, J. P., Bridges, D. W. and Fassell, W. M., *J. Electrochem. Soc.* **102**, 490 (1955).
- (5) Kofstad, P., *Nature (London)* **179**, 1362 (1957).
- (6) Kubaschewski and Hopkins, "Oxidation of Metals and Alloys" (Butterworths Scientific Publications, London, 1962), pp. 199-201.
- (7) Freeman, Eli Saul, Ph.D. Thesis, Rutgers Univ. (1961).
- (8) Laidler, K. J., "Chemical Kinetics" (McGraw-Hill Book Company Inc., New York, (1950), p. 76.
- (9) Kelley, K. K. and Anderson, C. T., U.S. Dept. Interior, Bur. Mines and Bull. 384 (1935).

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