

THE CHEMICAL KINETICS OF REDOX REACTIONS

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Abstract

Kinetics relations was determined by measuring gases and the assumption that the speed of development pressure is a measure of the rate of decomposition.

All decompositions solid phase curves give pressure - sigmoidal time. Such relationships are typical chain reactions and trying to interpret normal decomposition chain reactions theory.

This theory sufficiently take into account the existence of a well defined induction period was observed in some cases. Induction or delay period comprises a period of slow chemical reaction.

Autocatalysed existence in solid phase decomposition is well known and as noted in the examples above, that tetril, azides, ciclotrimetilnitramină etc.

This is due to the formation of an intermediate that is either liquid or lowers the melting point of the reactant. In such cases, the reaction being measured is that of the first reactant in a molten form or in solution saturated enter a product.

Because reagent decomposes much higher speed than in the solid liquid form, this effect is responsible for autocatalizarea observed in most organic solids, particularly when measurements are made near normal melting point.

So, it is interesting to compare the relative speed of decomposition of the same substance in solid and liquid phases.

Available data are summarized in Table 1. Although initial rate ratio in the two states is considerable, it is not as great as can be expected, given the greatly increased molecular mobility. An approximate value of the report may be obtained assuming that the difference in reactivity of a substance solid and liquid phases is due entirely to the difference in internal energy in the two states.

This is equal to the heat of fusion and thus a first-order reaction:

$$K_s = A_s l^{-E_s/RT}, \quad (1)$$

$$K_e = A_e l^{-E_l/RT}, \quad (2)$$

and

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$$\log \frac{K_l}{K_s} = \ln \frac{A_l}{A_s} + \frac{E_s - E_l}{RT}, \quad (3)$$

where E_s and E_l are the activation energies for the decomposition of solid phases respectively liquid and $E_s - E_l$ is equal to the latent heat of fusion per mol. For the majority of the latent heat of fusion of organic compounds is the field of compounds 10-50 cal / g. The molecular weight = 200 and latent heat 20 cal / g $E_s - E_l = 5000$ cal / mol and 100 ° C, this gives the K_l / K_s value of about 800 if $A_l = A_s$. In addition, this value must be a lower limit, because decomposition of the solid molecules may be restricted to those molecules in the vicinity of the surface layer.

Table 1.
Initial rates of decomposition in the solid state and liquid

Compound	Liquid phase		Solid phase		Speeds ratio
	log A	E	log A	E	
Tetril	15,4	38,4	12,7	36,6	30 la 100°C 60 la 120°C
Ciclo-trimetil-nitramină	17,7 18,5	45,5 47,5	16,7	45,5	10 la 200°C

Assuming that the decomposition is based on the crystal surface, then as shown by the more decomposition of the solid *Garner*, the number of molecules which decompose on the surface of the solid unit, the unit time is given by the reaction of *Polanzi - Wigner* (4)

$$K = N\nu e^{-E/RT}, \quad (4)$$

where ν a frequency factor is about 10^{13} sec⁻¹, but can be substantially increased.

N is the number of molecules per unit area of the crystal and E is the experimentally determined activation energy.

If it is assumed that the speed of decomposition is the initial velocity in the liquid phase, since most of the reactions was found that this is a first-order decay law, then:

$$-\frac{dn}{dt} = K_l n_o, \quad (4)$$

where K_l is the first order reaction constant, not the molar concentration because the variation in volume of the melt is low, the speed of decomposition in the solid phase:

$$-\frac{dn}{dt} = K_l n_o = \beta K_l n_o, \quad (5)$$

where β is the fraction of molecules in the solid surface:

$$\frac{K_s}{K_l} = \beta. \quad (6)$$

If the solid is considered as a cubic lattice and composed of small blocks, each side L , then after every molecule occupies a cube of length l ,

$$\beta = \frac{L}{6l}. \quad (7)$$

Representing the speed of decomposition of the solid by:

$$-\frac{dn}{dt} = Kl\beta n, \quad (8)$$

autocatalysis observed can be easily understood that β , the fraction of molecules that have not reacted, either in a region of the disturbance produced by decomposition or solution of the product molecules will increase to a maximum and then decreases during the reaction in the last stage. This model will give a pressure curve - sigmoidal temperature. The decrease in the value of the form will not occur if sufficient liquid to dissolve the reagent, and in such a case it is known that the decomposition follows closely a first order rate law.

Conclusion:

Thermal decomposition and transformation of explosives in the blast, accompanied by the release of a considerable energy as heat. If the rate of heat production is higher than the rate of heat loss to the environment by convection and conduction heating appears solid and the reaction is accelerated to a high speed, culminating in the ignition and explosion. This explosion is known as a "thermal explosion".

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