EXPERIMENTAL STUDY AND KINETIC MODELLING OF THE PRE-SPINODAL PROCESSES IN CONDENSED EXPLOSIONS AND REACTIVE SYSTEMS

O.F.Shlensky
Mendeleev University of Chemical Technology, Miusskaya sq,9, 125047 Moscow, Russia
FAX: (095)2004204, e-mail: mikl@shlensky.msk.ru

New optical interference method of investigation of the kinetics of thermolysis and evaporation of a thin layer of matter under the action of various external factors is elaborated. Appropriate mathematical models to describe the combustion processes with respect to existence of the upper boundary of the metastable state of condensed reactive systems have been suggested.

INTRODUCTION

The temperature of the reagents during the processes of combustion, ablation, laser material treating, etc. may be highly elevated and reach the upper temperature boundary of a metastable state, i.e. a spinodal line. The spinodal line parameters are determined from the equation of state with the aid of the condition of inner thermodynamic stability: the second variation of Gibbs free energy is equal to zero for a given material ($\delta^2 G = 0$).

Practically, it is difficult to reach the spinodal line during the experimental test especially for explosive matters. Early investigations have shown that at an attainable overheat (or limiting superheat) temperature T_{lim} in the vicinity of the spinodal line, the process of the homogeneous nucleation intensifies very much, the mechanisms of the chemical reactions can change, and the reactivity of products increases sharply. Near the temperature $T_{lim,}$ the reaction rates usually are higher than ones predicted on the basis of the Arrhenius monomial equation.

As a rule these pre-spinodal effects were not taken into account in the calculations of the combustion and explosion processes due to the absence of reliable experimental data and appropriate thermodynamic interpretation. Many of traditional methods of thermal analysis did not allow obtaining these data because the rates of sample heating are very low.

According to the early described [1,2] contact thermal analysis methods rapid heating is achieved by applying thin layers (2...7 mcm, (μm)) of an investigated material (sample) to a metal plate (substrate) which has been heated previously to a constant elevated temperature. The processes of pre-spinodal reactions can be observed, for example, from two-dimensional pictures recorded by means of a visible or infrared light TV camera and VTR. In order to obtain the actual values of thermolysis reaction rate it is usual to measure the weakening of luminosity of the sample from one frame to another consequently. Luminosity of sample is connected with optical properties and mass amount (film thickness) of the sample. The magnitude of T_{lim} is determined from the plot log(k) = f(1/T) for a given material on the metal plate at the temperature T. To obtain the plot log(k) = f(1/T) it is necessary to conduct 15-25 tests at different temperatures of the metal plate (T = const during the test) .By the contact method the attainable overheat temperatures of different kinds of polymers, olygomers, petroleum products, explosives, crystal hydrates, composites for thermal protection etc. were obtained.

The kinetics of the process of thermolysis and evaporation of thin layers of matter under condition of considerable superheat depends, to a certain extent, on the effects of various extremal physicak factors which, for example, are capable of varying the nucleation rate in superheated metastable matter and of promoting the emergence in matter of additional internal mechanical stresses and strains . The latter, in their turn, may become additional sensitizers of the development of the process of thermal decomposition. As a result, a possibility is opened up of controlling the process by proper selection of the parameters of external additional stimulation. The most commonly encountered external physical factors include the mechanical, sound, ultrasonic and electromagnetic vibrations excited in decomposing matter.

EXPERIMENTAL APPROACH

At present, the so-called replica technique is used to investigate the rate of evaporation and thermolysis of thin layers of matter. In this communication, we describe a new procedure for measuring the lifetime of superheated matter with the aim of optical interference method. This method allows to increase time resolution and to investigate the effects of sound and ultrasonic vibrations on the rate of the processes of thermolysis and evaporation of thin films of matter that are applied onto a substrate by replica technique.The procedure is based on recording the effects of scattering and interference of light in transparent and semitransparant media of small thickness. This procedure consists in the following. If a thin layer (10-20 mcm, in accordance with the replica method) of the material being investigated is applied onto a smooth pre-heated glass plate of finite thickness and such an optical system of film-glass substrate is illuminated by narrow-beam monochromatic laser radiation, the interference of light beams reflected from the glass and scattered in the film will occur in this system. In the absence of a film, the behavior of reflection from the smooth glass surface will be close to mirror reflection (reflection from the second face of glass is negligibly small, and in the presence of an applied and evaporating semitransparant film, a scattered interference component, nonstationary with respect to the solid angle and correlating with the thickness and optical properties of the film, will prevail in reflected radiation. If the lens of a photodetector is placed in the path of reflected radiation, with the mirror-reflected bean cut off by a small nontransparant esreen, only the scattered component will get to the photodetector; that is, the signal from the photodetector output will occur only in the presence of film on the substrate. Therefore, the shape of signal from the photodetector output as a function of time defines the period of time during which the film is on the substrate, i.e. th film lifetime. Theoretically, in such a scheme, the time resolution is limited only by the inertia of the photodetector and recorder and may be less than 1 mcs.

The experiment performs in the following manner. A film of the material being investigated is applied onto a glass substrate placed on an inertial heater. The site of film application is illuminated by a beam of a He-Ne laser. Reflected radiation passes through a set of optical filters designed to cut off background illumination, in particular, hear radiation, from the heater, and gets onto a lens of a photodetector. The mirror- reflected beam is blocked by a point screen. The electric signal from the photodetector output is amplified by an instrumentation amplifier and delivered for digitization, recording, and processing to a personal computer provided with a suitable interface to an analog-to-digital converter and software. In order to deliver external mechanical and acoustic vibrations, the glass substrate is connected by a glass rode to a replaceable ultrasonic (sound) radiatior serving as the load of a high-power wide-range electric oscillator assembled on the basis of a standard G5-56 generator.

The replaceable ultrasonic radiators are provided by a set of piezoceramic transducers of barium titanate. The characteristic feature of operation of these transducers is that the maximun amplitudes for longitudinal and transverse vibrations are possible only for two respective resonance frequencies determined by the geometric dimensions of the transducer plate and by the respective rates of propagation of longitudinal and transverse waves in the plate material. In realty, we have a more complex acoustic system including a radiator, a rod, a substrate, and a film, this system having its own set of resonance frequencies. Note that the latter set of resonance frequencies depends on the thickness and acoustic properties of the film being investigated, which vary with time, the system being further characterized by pronounced decay. Because of this, it is almost impossible to calculate the amplitude-frequency characteristic of such a system. Experimentally, the amplitude-frequency characteristic may be readily determined only for the radiator plate, by way of measuring the modulus of electric impedance. However, the use in the rod-sibstrate transmitting system of materials, whose rate of propagation of longitudinal sound waves is close to that of the radiator plate, in combination wich the use of a higher-power oscillator, facilitates the solution of the problem considerably, For example, in the case of barium titanate, flint and light flint glasses were used, with the rates of longitudinal wave propagation amounting to 4500, 4260 and 4800 m/s.

In the table 1 some previous and new experimental data are presented

Table 1.The values of attainable (limiting) overheat temperatures T_{lim} of some materials

Sample	T_{lim} ^{0}C	Sample	T_{lim} ^{0}C
Polystyrene(block)	530	Sodium azide	550
Polystyrene(impact resistant)	540	Lead azide	395
Polyvinyl chloride	470	Cadmium azide	340
Polyethylene terephthalate	500	Mercury azide	425
Polyethylene (high dens.)	515	Glycerine	460
Polyethylene (low dens.)	500	Nitroglycerin	280
Polymethylmetacrillate	515	Ammonium nitrate	340
Nitrocellulose	320	Ammonium perchlorate	495
Coal (for the gasificaton.)	529	Ammonium dichromate	295
Borax	380	Octogen	350
Colemanite (mineral)	395	Trinitrotoluene	350
Naphtha (of the Alaninsk seam)	500	TATB	460
Isoprene caoutchouc (SKI-Rubber)	720	Polydiethylsiloxane (PES-4)	522

THERMODYNAMIC MODELS

The calculation of saturated vapor pressure is based on the Clapeyron-Klausius equation: $dp/dt = \Delta H/T(V_g-V_c)$, where V_g, V_c are gas and condensed phase volumes. For evaporation or sublimation processes (assuming $V_g = RT/p >> V_c$) we have $dp/dt = \Delta H/RT^2$. This equation is free of any temperature limitation. It is valid far from spinodal line. In the vicinity of spinodal line V_g is comparable with V_c and the assumption $V_g>>V_c$ is invalid. The dependence $V_c(T)$ is determined by the equation of state, but its using make difficult as a rule the procedure of integration. With the aid of an simple offered approximate function F(T) we have: V_g-V_c = = RTF(T)/p, where F(T) = $(1-T/T_l)^m$, (m<0) or F(T) = $1-(T/T_l)^n$, (n>0) that allow to fulfill the integration procedure . After transforms we have p = Bexp(-ΔH(1-Δ)/RT), where Δ is a spinodal correction. For example, if n = 2, Δ = $(T/2T_l)\ln[(1+T/T_l)/(1-T/T_l)]$. With the aid of similar approximate function from the thermodynamic equation for the chemical potential $\mu = \mu_* +\int Vdp$, where μ* is integration constant after integration and transformations we obtain the simple relationship for the temperature dependence of equilibrium constant (see the table 2).

KINETIC MODELS

The discovery of attainable overheat (superheat) temperatures of various condensed substances is very important for combustion theory since it forces reexamination of many existing mathematical models of processes taking place at intensive heating. Instead of ordinary monomial Arrhenius equation k = z exp(-E/RT) witch is valid strictly speaking for gaseous mixtures only) it is necessary to use a complex shaped function of many variables and parameters: k = F(k_{hom}; k_{het}; k_{hem}; D; T_{lim} ...) where k_{hom}, k_{het} are frequencies of homogeneous and heterogeneous nucleation , respectively, k_{chem} is a true chemical reaction rate and D is a diffusion coefficient.

For example, in the case of one-stage of nucleation it has been established in [3] $k = C[k_{hom} + k_{het}]^{\beta} [k_{chem}]^{\lambda}$, where C,β,λ are parameters, $k_{hom} = k_1\exp(-E_{hom}/RT)$; $k_{ht} = k_2\exp(-E_{het}/RT)$; $k_{chem}=k_3\exp(-E_{chem}/RT)$.

It is difficult to determine all 9 parameters ($C,\beta,\lambda,k_1,k_2,k_3,E_{hom},E_{het},E_{chem}$) of above equations from experimental data because this problem is mathematically uncorrected. The digital computations showed that in some cases modeling of combustion, coking of coals and thermoreactive polymers, ablation of thermal protection etc. satisfactory results can be obtained if more simple equation are applicated [3,4], for example, the next approximations can be used: $k = z \exp[-E(1-T/T_{lim})^n/RT]$, $k = z \exp[(-E/RT) + C/(1-T/T_{lim}+d)]$, where z,C,n,d are parameters (n ≅0,01).

Taking into account the pre-spinodal effects, new equation for adiabatic induction delay of explosive selfignition, the combustion front propagation velocity with intensive heating, velocity of process of thermal decomposition at low-rate detonation and explosion generation condition at slight mechanical action etc. have been described. Some expressions are presented below in the table 2.

Table 2. Comparison of some characteristic traditional and suggested equations

Well known equations for mathematical simulation (free of any temperature limitations)	Advanced (suggested) corrected equations for mathematical simulation (with respect to temperature spinodal limitation)
1. The saturation vapor pressure expression	
Differential form	
$d(\ln p)/dT = \Delta H/RT^2$	$d(\ln p)/dT = \Delta H/RT^2F(T)$, where F(T) is correction for spinodal
Integral form	
$p = B\exp(-\Delta H/RT)$	$p = B\exp(-\Delta H(1-\Delta)$, where Δ is correction for spinodal
2. The temperature function for equilibrium constant	
$K_p = A\exp(-\Delta H_{ch}/RT)$	$K_p = A\exp(-\Delta H(1-\Delta)/RT$, where Δ is correction for spinodal
3. The single-stage kinetic equation for thermolysis	
$dc/dt = z\exp(-E/RT)c^m$	$dc/dt = z\exp[-E(1-T/T_{lim})^n/RT]c^m$
4. Adiabatic ignition delay (induction period of self-ignition)	
$t_{ad} = \frac{c}{zQ}\int_T^{\infty}\exp\left(\frac{E}{RT}\right)dT = \frac{cRT}{zQE}\exp\left(\frac{E}{RT}\right)$	$t_{ad} = \frac{c}{zQ}\int_T^{T_{\lim}}\exp\left(\frac{E}{RT}\right)dT \approx \frac{cRT}{zQE}\left(1-\exp\left(-\frac{E(T_{\lim}-T)}{RT}\right)\right)\exp\left(\frac{E}{RT}\right)$
5. Propagation velocity of the combustion front	
$u = \sqrt{\frac{2Kz}{Q}\int_T^{T_{final}}\exp\left(-\frac{E}{RT}\right)dT}$	$u = \sqrt{\frac{2Kz}{Q}\int_T^{T_{\lim}}\exp\left(-\frac{E(1-T/T_{\lim})^n}{RT}\right)dT}$

6. Heat release function

$W(T) = Q\,z\,\exp(-E/RT)c^m$ | $W(T, p) = Q\,z\,\exp[-E(1-T/T_{lim}(p))^n/RT]c^m$

Comparison of some calculations was made with use of the left column equations and with the right column equations. It shows that the difference between their results may reach two or three orders of magnitude, especially in the high temperatures region near temperature T_{lim} (in the vicinity of the spinodal line). At the same time the calculation results obtained satisfactory are confirmed with both our and literature experimental date, see [1,2,4,5].

CONCLUSION

Every condensed substance, including explosives, has an upper temperature boundary of their existence in the metastable state, i.e. the spinodal line. Near the spinodal line every condensed system transmutes into labile (unstable) state, i.e., will be collapsed. The present day theory of combustion and explosion has been elaborated earlier for the gas phase (gas mixtures) only, which has neither spinodal nor spinodal collapse. Therefore, the "gas theory" does not take into consideration any pre-spinodal physical or chemical effects (boundary temperature limits of any physical properties: density, conductivity, heat capacity heat release, etc.). The "gas theory" is especially invalid in the vicinity of the spinodal line. The concept suggested here overcomes this drawback and provides correct and adequate physical and mathematical models for condensed systems and combustion.

It is necessary to note that the chemical prespinodal effects established here different from the well - studied physical pre-spinodal effects which take place at the phase (liquid-vapor) transformations. Some of the more important conclusion of this work are:

1. The attainable overheat temperatures of some combustible and explosive materials have been determined with the aid of the new contact method of thermal analysis for the first time. Thereby the unknown thermodynamic property of substances has been established. New optical interference method has been suggested in this communication. It has more high resolution time than earlier described procedure.

2. The results obtained allow developing the new physics and mathematical models which are adequate for the actual processes in condensed matter (propellants, explosives, thermal protection layers etc.). Some of such models have been shown with its thermodynamic reasons.

3. The attainable overheat temperature T_{lim} of nonvolatile explosives corresponds to their ignition temperature T_{ign} in the case when the sample mass m, is finitely small: $\lim T_{ign} \Rightarrow T_{lim}$ at $(m \rightarrow 0)$.Therefore T_{lim} may be considered and used as the individual parameter of explosion hazard.

4. The behavior of the chemical pre-spinodal effects allows establishing the non-empirical functions and relationships of reaction rates and the explosive probabilities in the connection with slight mechanical action: mechanical stresses, shift waves, vibration ultrasound input, impact loading, friction, etc.(See the second communication). The understanding of the nature of mechanical tension makes it easily to regulate the sensitivity of the explosives.

5. The growth of reagents reactivity near the spinodal line may be employed for the improvement of the intensive technologies (laser and plasma treatment, SNS, high temperature cracking etc.) Understanding of the role of surface tension at thermolysis processes allows properly to select the stabilizers (flegmatilisers) and sensibilisers of explosives taking into account the nucleation frequency.

ACKNOWLEDGMENT

The research described in this publication has been made possible in part by Grant no. 96-02-17639 from Russian Foundation for Basic Research.

REFERENCES

1. O. F. Shlensky, (1996) Pre-spinodal effects and their role in dynamics of condensed reactive systems, Combustion Science and Technology, Vol. 120, pp. 383-391.
2. D. N.Yundev, D. A. Rogatkin, and L. G. Moiseeva, (1998) , High Temperature, Vol. 36, No. 1. pp. 160 – 162. (Transl. from Teplofisika Visokikh Temperatur Vol. 36, No, 1, pp. 161 - 164).
3. M. Braun, D. Dollimor, A. Galwey, (1980) Comprehensive Chemical Kinetic, ELSEVIER, 350 pp.
4. O. F. Shlensky et. al., (1991) Thermal Decomposition of Materials, ELSEVIER, 302 p..
5. O. F. Shlensky, (1998) Chemical Physics Reports, Vol. 17, No. 4, pp 116 - 119.