J Therm Anal Calorim (2011) 103:471–472
DOI 10.1007/s10973-010-0921-7

Equivalent isothermal curves for kinetic analysis of non-stoichiometry

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Received: 9 April 2010 / Accepted: 9 June 2010 / Published online: 24 June 2010

Abstract The author proposed a method for analyzing kinetics of non-stoichiometry by observing cyclic mass change behavior under cyclic temperature change. Because relationship between the mass and the mass change rate is independent on the previous thermal history of the specimen, we can get equivalent isothermal curves (synthesized isothermal curves) by extracting datum pairs of mass and mass change rate at a given temperature and many conversions, changing the frequencies. The equivalent isothermal curves are really the same as curves of conversion and rate of conversion observed isothermally, so that conventional methods for kinetic analysis can be similarly applied to the equivalent isothermal curves. When multiple elementary processes are proceeding, they can be separately observed by changing the frequency, so that, the method proposed in this short communication is useful and effective to elucidate kinetics of non-stoichiometry as well as reversible reactions.

Keywords Non-stoichiometry · Kinetics · Equivalent isothermal curves · Synthesized isothermal curves · Cyclic temperature change · Cyclic mass change · $YBa_2Cu_3O_{7-\delta}$

In a precious paper [1] the author reported mass change behavior of non-stoichiometric compound, $YBa_2Cu_3O_{7-\delta}$ under cyclic temperature change. When this substance is heated and cooled at very low temperature frequency, namely at very low rates of heating and cooling, the mass change follows the equilibrium change instantaneously without time lag, so that when we plot the mass change versus the temperature, the data obtained in heating mode and those in cooling mode are all on a single same curve of the equilibrium. When we increases the temperature frequency to a certain extent, the mass change does not follow the equilibrium because the temperature change is fast, while the mass change takes a certain time. The mass change cycle oscillates with some detectable delay and the mass change follows the equilibrium with a time lag. Thus, when we plot these data of the mass versus the temperature, we get an elliptic curve, and the data moves on this elliptic curve clock-wisely by heating and cooling; the upper curve is that for heating mode and the lower curve for cooing mode. When the frequency is increased much more enough, the mass change does not occur and it is fixed at a certain value. Thus, we have a parallel line with the abscissa.

To discuss the above mass change behavior in more quantitative way, the author [1] proposed a fundamental kinetic equation, i.e.,

$$\mathrm{d}m/\mathrm{d}t = -k(m - m_\mathrm{e}) \tag{1}$$

where m, t, k, and m_e are the mass of the specimen, the time, the rate constant, and the equilibrium mass, respectively. The driving force of the mass change is the difference between the actual mass and the equilibrium mass. For simplicity, k is assumed constant, i.e., it is independent on the temperature, though it is not so in reality. It is also assumed that k in the heating mode is equal to that in the cooling mode. The equilibrium mass is also assumed to be linearly dependent on the temperature. Solving the above equation on condition that the temperature changes in a sine wave, we get amplitude and time lag of the cyclic mass change, and it is the same as described above [1]. It is

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also made clear that the maximum time lag occurs when the frequency is comparable with the rate constant.

This cyclic mass change is very useful to observe non-stoichiometry. For instance [1], when we observe non-stoichiometry of $YBa_2Cu_3O_{7-\delta}$ in the above described way, we found that there occur three different oxygen sites in the crystal and their behaviors of oxygen absorption and release are quite different from each other. In this particular way of the cyclic temperature change, oxygen and crystalline three sites behave quite differently. Among three, one shows annealing behavior of gradual mass increase. These behaviors cannot be observed separately by other temperature modes, such as isothermal observation or at a constant rate heating and/or cooling.

However, the above way of observation is not enough, because the rate constant is assumed constant, so that the really observed curves would be somewhat deformed from that descried above. Furthermore, we cannot observe the temperature dependence of the rate constants. Thus, the method to discuss the temperature dependences of the rate constant is quite important, and the rigorous quantitative analysis bring us much more detailed information, for instant to discuss the quenched crystalline glassy state. The author recently found a different way to observe the rate constant in more detail. A new concept of equivalent isothermal curves [2–4], which were applied to thermal decomposition of polymers, is also useful in the non-stoichiometry observation. In the case that only a single process is involved, the following equation holds.

$$dx/dt = kf(x) \tag{2}$$

where x and $f(x)$ are the extent of the conversion and a single valued function of x, respectively. One of the important point of this equation is that it is not dependent on previous thermal history of the specimen under observation, so that if we get combined data of conversion and rate of conversion at a given temperature, we get plots, which are equivalent to the curve of conversion versus conversion rate obtained by isothermal observation. We can also use data obtained by cyclic temperature change and/or data obtained by different runs of different temperature program. Thus, non-isothermal data obtained by various temperature modes can be transformed to isothermal curve. The equivalent isothermal curves thus obtained can be analyzed by conventional methods to kinetically analyze conventional isothermal data. One of prerequisites for this kinetic analysis is to get data of conversion rate of high accuracy.

Thus if we observe the non-stoichiometry by changing temperature frequency and extract combined data of conversion and rate of conversion at given temperatures, the rate constant and its temperature dependence are able to be estimated by analyzing thus obtained equivalent isothermal curves. As was seen in the previous paper, the specimen of non-stoichiometric oxygen contents tends to be quenched and it might freeze to glassy crystalline state. To investigate this interesting behavior, the above kinetic analysis would provide us with useful information. Furthermore, as is clearly shown in the above case of $YBa_2Cu_3O_{7-\delta,}$ we can observe a single process separately with the others, so that we can also analyzed equivalent isothermal curves similarly.

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