The kinetics of the thermal decomposition of the cubic ammonium perchlorate (AP) has been extensively studied. The reported effective activation energies vary from about 371 to 260 kJ mol\(^{-1}\). The mechanistic interpretation of the values is also different. The confusing character of the kinetic information is not surprising for the process that is known\(^3\) to be a tangled interplay of various chemical (solid-state decomposition, reaction of gaseous products with the solid, gas-phase reactions) and physical (diffusion, sublimation, adsorption-desorption) processes. The effective activation energy of the thermal decomposition of AP is a composite value determined by the activation energies of these processes as well as by their relative contributions into the overall decomposition rate. If these processes have different activation energies, the effective activation energy shows a variation with the temperature. The kinetics of such multi-step processes cannot be characterized by a single constant value of the activation energy. The latter is traditionally evaluated by equation 1:

\[
\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha)
\]

where A (preexponential factor) and E (the activation energy) are Arrhenius parameters, \(\alpha\) is the extent of conversion, \(f(\alpha)\) is the reaction model, \(t\) is the time, \(T\) is the temperature, and \(R\) is the gas constant. The earlier kinetic evaluations of the activation energies of the thermal decomposition of AP were based on the assumption of a constant activation energy. The isocconversional method, which is the basis of Mettler-Toledo’s kinetic software “Model Free Kinetics”,\(^4\) allows one to reveal the dependence of the activation energy on the extent of conversion and/or on the temperature. The analysis of such a dependence is usually very helpful in drawing mechanistic conclusions about the process\(^5\). In this study, we apply the model free kinetic analysis to TGA data on the thermal decomposition of cubic AP. AP (Aldrich) was used as supplied.

The thermogravimetric analysis (TGA) experiments were carried out using a TGA/SDTA851\(^{\circ}\) instrument. Samples of AP were placed in aluminum pans and heated in a flowing atmosphere of nitrogen (100 ml/min). The TG experiments were carried out at heating rates 5, 7.5, 10, 12.5, and 15 °C/min.

At 240 °C DSC curves (Figure 1) show an endothermic peak corresponding to the transformation of AP from orthorhombic to cubic form. It is followed by an exothermic feature due to the thermal decomposition. The thermal behavior of AP is markedly different in open and closed pans. In a closed pan, the thermal decomposition of AP is completely exothermic. In an open pan, the exothermic decomposition is overtaken in the

![DSC curves of AP](image)

Fig. 1: DSC curves of AP at a heating rate of 5 K/min in hermetically sealed and in Al standard crucibles with pierced lids. At 250 °C the solid-solid transition to the cubic modification occurs. Decomposition reactions follow afterwards.
later stage by an endothermic event. Analysis of the literature DTA/DSC data\textsuperscript{6,7} shows that the second peak appears as exothermic under conditions that retard the escape of reaction gases. Conversely, under conditions that facilitate the removal of gaseous products the second event appears as an endothermic peak which is attributed to dissociative sublimation of AP to ammonia and perchloric acid. By comparing DSC and TG curves (Figures 1 and 2) we can see that the point when decomposition turns into endothermic stage is perfectly correlated with the slowdown ($\alpha = 0.30$ to 0.35) observed in TG experiments. The 30\% to 35\% decomposed AP has a highly porous structure\textsuperscript{8}. Therefore, the solid-state thermal decomposition of AP involves two major stages. The first stage ($\alpha < 0.3$) is exothermic decomposition that results in formation of porous AP. The second stage is endothermic dissociative sublimation of AP. Sublimation and exothermic decomposition are most likely to occur throughout the whole process. The two major steps of the decomposition are mirrored in the dependence of the activation energy on the extent of conversion (Figure 3). The exothermic decomposition ($\alpha = 0$ to 0.3) results in development of the high surface area that favors physical processes of diffusion and adsorption and that hinder the escape of gaseous decomposition products. As a result, the exothermic decomposition becomes controlled by the slow mass-transfer processes which are characterized by low activation energies. This explains slowing the mass loss process (Figure 2) as well as decreasing the effective activation energy (Figure 3) while $\alpha$ increases to 0.3. At small extents of conversion, the process is kinetically controlled. The effective
value of the activation energy $E_A$ (115 kJ mol$^{-1}$) is an estimate for the activation energy of the thermal decomposition of AP. At $\alpha = 0.3$, the exothermic decomposition still prevails over sublimation but slows down markedly. Therefore, the effective value of the activation energy $E_A$ (80 kJ mol$^{-1}$) can be used as an estimate for the activation energy of the mass transfer process responsible for the removal of gaseous products. The development of the high surface area promotes transformation of the process from the exothermic to the endothermic regime at $\alpha > 0.3$. The rate of sublimation is directly proportional to the surface area. According to some data$^9$, the surface area of the 30% to 35% decomposed AP is 1000 times greater than that of the original AP. Then, we may expect that by $\alpha = 0.3$ the sublimation increases 1000 times as compared to that at the beginning of the decomposition. This seems to be the major reason why sublimation ultimately takes over the slow exothermic decomposition controlled by mass-transfer. Nevertheless the exothermic decomposition is most likely to accompany sublimation. The coexistence of these two processes is supported by the fact that the endothermic effect estimated by DSC (140 kJ mol$^{-1}$ after correcting for the initial mass loss) is only about 60% of the experimentally determined$^{10}$ enthalpy of sublimation, $242 \pm 0.8$ kJ mol$^{-1}$. Because the activation energy of sublimation (125 kJ mol$^{-1}$) is greater than that for the mass-transfer controlled decomposition (about 80 kJ mol$^{-1}$), the relative contribution of the sublimation into the overall process rate increases with the temperature. Consequently, the effective value of the activation energy $E_A$ (125 kJ mol$^{-1}$) that corresponds to the maximum temperature should be used as an estimate for the activation energy of sublimation. In accord with earlier theoretical and experimental findings$^{11}$, this value is about one-half the enthalpy of sublimation. Therefore we can propose a relatively simple kinetic scheme for the thermal decomposition of cubic AP:

This example shows how model free kinetics can assist the clarification of reaction mechanisms.

References
4 Kelsey, M. S. Am. Lab., January, 1996, p. 13, Datenblatt Modellfreie Kinetik (ME 51 724 783)