

S.I. 1: Enthalpy-Entropy Compensation in Activated Processes Described Using the Eyring Equation

Combining Eq. 1 and Eq. 12 yields:

$$k = e^{\left[a + bE - \left(\frac{E}{RT} \right) \right]} \quad (A1)$$

From Eq. A1, one can infer that there are two components of the activation energy – one that has the expected T -dependence from Eq. 1 and the other that is a constant (T -independent), but whose magnitude is modified by the coefficient, b , rather than being normalized to RT in the Arrhenius manner. To better understand the latter result, one can turn to the Eyring equation and replace E in Eq. 1 with the Gibbs free energy of the barrier to activation, ΔG^\ddagger ($= \Delta H^\ddagger - T\Delta S^\ddagger$):

$$k = \frac{\kappa k_B T}{h} e^{\frac{\Delta S^\ddagger}{R}} e^{\frac{-\Delta H^\ddagger}{RT}} = \frac{\kappa k_B T}{h} e^{\frac{-\Delta G^\ddagger}{RT}} = \frac{\kappa k_B T}{h} K^\ddagger \quad (A2)$$

where κ is the transmission coefficient, k_B is the Boltzmann constant and h is the Planck constant. According to Transition State Theory, there exists a quasi-equilibrium (specified by the constant, K^\ddagger) between the reactants and the transition state species that defines the barrier height, taking into consideration the partition functions of the relevant species. From Eq. A2, one finds that $k = 1$ specifically

when $K^\ddagger = \frac{h}{\kappa k_B T}$. Therefore, applying this simplifying condition, a valid result is:

$$\Delta H^\ddagger \approx T \left\{ \Delta S^\ddagger + R \left[\ln \left(\frac{\kappa k_B T}{h} \right) \right] \right\} \quad (A3)$$

Generalizing Eq. A3 (to make it valid for other constant values of k), allows one to obtain the familiar result for kinetic enthalpy-entropy compensation (for a given mechanism and at fixed T, P):

$$\Delta H^\ddagger = c + d\Delta S^\ddagger \quad (A4)$$

whereby one introduces the new, empirical constants, $c \approx RT \left[\ln \left(\frac{\kappa k_B T}{h} \right) \right]$ and $d \approx T$. The latter constant has been used by some workers to infer the isokinetic temperature and, from it, the apparent (approximate) transition state dissociation frequency. However, Eq. 4 should generally be applied with caution because, while it has been discussed previously that entropy-enthalpy compensation is not the same thing as an isokinetic relationship (one does not necessarily support the existence of the other), both relationships are often plagued with “artifacts and misunderstandings”¹¹ and, as could be the case in solid-state kinetics, “misuse of the kinetic model can lead to compensation”¹¹ since the difference in the magnitude of experimental error often associated with A and E in Eq. 12 can make observed correlations dubious from a statistical viewpoint. For this reason, the *a priori* assumption of a compensation effect, as an integral part of any thermal method, could warrant further justification.

Regardless, for the sake of completeness, using the same assumption ($k = 1$) in Eq. 1 yields:

$$\ln \frac{d\ln \frac{A}{A_0}}{d\ln \frac{P}{P_0}} = \frac{E}{RT} \quad (A5)$$

from which, by analogy to Eq. A4, one can derive the general functional form of Eq. 12 (whereby the non-

zero constant, a , is added to accommodate empirical curve-fitting and $b \approx \frac{1}{RT}$).

S.I. 2: Dispersive Kinetics

The distribution of activation energies underpinning DKMs⁷⁻⁹ comes about due to distributed reactivity¹⁰. Most simply, one can consider this behavior to be attributable to a multi-step conversion in which the mechanism is fixed but perturbed slightly from one molecule to the next. Although chemically

identical, molecules within a condensed phase can experience different environments depending on their spatial location within the crystal, the size and shape of the primary particles, lattice defects, agglomeration, etc., that can cause them to react at different times and/or with different specific rates. Moreover, these factors often evolve continuously over the course of the conversion. The resultant dynamical contribution to the underlying conversion kinetics, which (coarse-grained) gives the activation energy distribution its width, is often unnoticed in the case of a well-stirred solution whereby all dissolved molecules undergo conversion with the same specific rate due to the similarity of their environment. Consequently, DKMs also exhibit a time-dependent k , whereas in CKMs it is generally a constant (per the Arrhenius equation).

Dispersive kinetics have been described using the concept of fractal reactivity⁸. While geometric fractals are well-known, describing the change in k of a solid-state conversion using fractals is, perhaps, most simply understood by considering that particles of varying size will require different durations to complete conversion. In addition to that, while molecules on the surface will convert with a different rate than those in the bulk, new surfaces can be expected to be generated continuously over the course of the conversion via “system renewals”⁸. Therefore, even for a unimodal particle size distribution of fixed size, one can think of distributed reactivity through the implicit assignment of a different rate constant to different “layers” of molecules in the particle, considering it to be akin to an onion¹². This is particularly important on the nanometer dimensions of nuclei and colloids, whereby relatively large energy differences might be expected between the individual layers (note that the “nowhere-differentiable” property common to fractals might lend support to the idea of quantization¹³). Contrastingly, as CKMs (or combined CKMs¹⁴) do not allow one to differentiate amongst the various environments in condensed matter by considering just a single (mean) specific rate for each elementary step of the overall conversion, they are often better applied to chemical reactions in the solution phase on most time-scales.