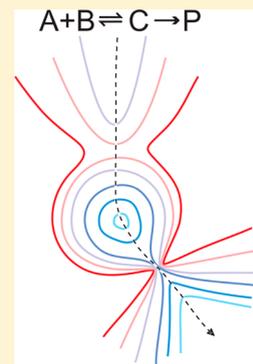


## Why Are Some Reactions Slower at Higher Temperatures?

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**ABSTRACT:** It is well understood by most chemistry students at advanced undergraduate levels that chemical reactions generally follow the Arrhenius law of temperature dependence with positive activation energies, proceeding faster at elevated temperatures. It is much less widely known that the rates of some Arrhenius-compliant reactions are retarded by increasing the temperature and are therefore associated with negative activation energies. The few readily accessible explanations of this phenomenon are rather cursory and limited to enthalpic considerations relating to the relative activation energies and thermicities of the component elementary steps of the process. However, these explanations are incomplete and consequently counterintuitive. Here we provide the required augmentation via entropic considerations.



**KEYWORDS:** Upper-Division Undergraduate, Physical Chemistry, Analogies/Transfer, Textbooks/Reference Books, Kinetics

The temperature dependence of the rate coefficients (and hence the rates) of most types of chemical reactions in most phases can be represented by the Arrhenius equation:

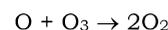
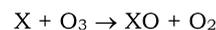
$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (1)$$

Here  $k$  is the rate coefficient,  $A$  is an intrinsically positive pre-exponential (or frequency) factor,  $E_a$  is the (molar) activation energy,  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and  $T$  is the absolute temperature. It is worth noting that eq 1 is strictly empirical;<sup>1</sup> for example, even simple versions of collision theory and transition-state theory predict that  $A$  and  $E_a$  vary (weakly) with temperature. Nevertheless, it is usual that eq 1 fits data more than adequately over substantial temperature ranges. Furthermore, the pre-exponential factor is only weakly temperature dependent, so the overall sense of the temperature dependence (whether the rate increases or decreases at higher temperature) is determined by the exponential term and hence the sign of the activation energy.

For the vast majority of chemical processes, reaction rates increase at higher temperature, corresponding to positive activation energies. In fact, it is the intuitive experience of us all that chemical processes are generally accelerated by heating (albeit at the risk of initiating other undesirable side reactions). But it is an under-recognized fact that some reactions actually proceed more slowly at higher temperatures and therefore correspond to effectively negative activation energies. An Internet search for the term “negative activation energy” yields a small host of sometimes amusing and occasionally bizarre, quasi-scientific statements as to whether negative activation energies can really exist, how they might come about, and what they really mean. Chemistry textbooks generally either disregard the possibility or devote to it little more than cursory comment as part of the discussion of complex reaction

mechanisms.<sup>2,3</sup> However, reactions of this type do exist,<sup>4,5</sup> and some of them are important to our environment, as illustrated by the following examples.

Stratospheric ozone depletion is commonly associated with the Antarctic ozone hole, which forms in the southern hemisphere’s late winter or early spring due to heterogeneous reactions involving chlorine and bromine species on the surfaces of polar stratospheric clouds. But it also occurs outside polar latitudes via homogeneous gas-phase reactions that are catalyzed by nitrogen, hydrogen, chlorine (and to a lesser extent, bromine)-containing species. The globally dominant ozone-depleting reactions are cycles of the form<sup>6</sup>



where  $X = \text{NO}$ ,  $\text{OH}$ , or  $\text{Cl}$ . The rate-determining steps (in bold) for all three of these cycles, have *negative* activation energies with  $E_a/R = -210$ ,  $-200$ , and  $-85 \text{ K}$ , respectively, for  $\text{NO}_2 + \text{O}$ ,  $\text{HO}_2 + \text{O}$ , and  $\text{ClO} + \text{O}$ .<sup>7</sup> The rate of ozone destruction due to the chlorine cycle should decline through the 21st century as concentrations of stratospheric chlorine-containing species diminish in accord with the Montreal Protocol for Substances that Deplete the Ozone Layer. However, concentrations of nitrogen- and hydrogen-containing species, and hence their contributions to ozone depletion (via the above cycle with  $X = \text{NO}$  and  $\text{OH}$ , respectively), are projected to increase following anthropogenic enhancement of the concentrations of their sources, the greenhouse gases nitrous oxide ( $\text{N}_2\text{O}$ ) and methane ( $\text{CH}_4$ ), respectively.

It is well established that increased greenhouse gas concentrations lead to a general warming of the troposphere

Table 1. Kinetics Expressions for Elementary Steps of a Reaction with a Potentially Negative Activation Energy

Step	Reaction	Rate Law	Arrhenius Expression
Forward step 1	$A + B \rightarrow C$	$v_1 = k_1[A][B]$	$k_1 = A_1 \exp\left(\frac{-E_1}{RT}\right)$
Reverse step 1	$C \rightarrow A + B$	$v_{-1} = k_{-1}[C]$	$k_{-1} = A_{-1} \exp\left(\frac{-E_{-1}}{RT}\right)$
Step 2	$C \rightarrow P$	$v_2 = k_2[C]$	$k_2 = A_2 \exp\left(\frac{-E_2}{RT}\right)$

because these gases are absorbers of infrared radiation. However, it is also true (although, perhaps, not well recognized) that such gases cause a concomitant *decrease* in the temperature of the stratosphere<sup>8</sup> because they are equally effective emitters of infrared radiation, which is lost to space from higher altitudes. Consequently, general circulation models project that the stratosphere is cooling and will continue to do so over the 21st century. A counterintuitive consequence of this cooling is that it will actually *accelerate* the rates of the ozone depleting  $\text{NO}_2 + \text{O}$ ,  $\text{HO}_2 + \text{O}$ , and  $\text{ClO} + \text{O}$  cycles due to the negative activation energies of their rate-determining steps.

These examples illustrate (a small part of) the complexity of terrestrial atmospheric chemistry and the challenges inherent in forecasting future trends and the mitigation of ozone depletion and climate change. But the subject of this communication is not atmospheric chemistry. Instead, we attempt here to bring some clarity to the concept of negative activation energies, how they arise and what they actually mean.

### ■ THE ENTHALPIC EXPLICATION

Consider species A and B that react to give products represented by P at a rate whose rate law is consistent with the kinetics of an elementary (single-step) bimolecular, reaction,



$v$  is the reaction rate and  $[A]$  and  $[B]$  are the appropriate activities (concentrations or partial pressures) of species A and B. The rate coefficient,  $k$ , obeys Arrhenius behavior (eq 1), but it diminishes with increasing temperature, meaning that  $E_a$  is negative. This latter result is incompatible with an elementary process, which (by definition) occurs in a single, coherent step, surmounting a single activation barrier with an inherently positive activation energy.

The conventional way of resolving this dilemma is to assume that the reaction proceeds via a complex mechanism of the sort<sup>2,3</sup>



Each of the three elementary steps that comprise this mechanism has an elementary rate law that is consistent with its molecularity and conforms to Arrhenius behavior with positive activation energy, as summarized in Table 1.

Step 2 of Table 1 is rate determining to the extent that  $v_{-1} \gg v_2$ ; in other words, intermediate C is much more likely to return to the reactants than it is to go on to the products. Because the rates of both of these reactions depend linearly on  $[C]$ ,  $v_{-1} \gg v_2$  requires  $k_{-1} \gg k_2$ , which in turn requires at least one of the conditions  $E_2 > E_{-1}$  and  $A_{-1} \gg A_2$  to be met. As will be seen, the first of these conditions is enthalpic, corresponding to the case where step 2 has a larger activation barrier. The second condition is entropic and corresponds to the case where

the configurational space around C is better suited for the reverse of step 1 to occur than it is for step 2 to occur.

Because  $v_{-1} \gg v_2$ , a condition of “pre-equilibrium” will be established between A, B, and C with an associated equilibrium constant given by

$$\begin{aligned} K_1 &= \frac{[C]}{[A][B]} = \frac{k_1}{k_{-1}} = \exp\left(\frac{-\Delta G^\circ_1}{RT}\right) \\ &= \exp\left(\frac{\Delta S^\circ_1}{R}\right) \exp\left(\frac{-\Delta H^\circ_1}{RT}\right) \end{aligned} \quad (4)$$

where  $\Delta G^\circ_1$ ,  $\Delta S^\circ_1$ , and  $\Delta H^\circ_1$  are, respectively, the standard molar Gibbs energy, entropy, and enthalpy changes associated with step 1. Additionally, because step 2 is rate determining, the overall rate for the mechanism in eq 3 is

$$v = v_2 = k_2[C] = k_2K_1[A][B] \quad (5)$$

Thus, the bimolecular rate law of eq 2 is obtained with

$$k = k_2K_1 = A_2 \exp\left(\frac{\Delta S^\circ_1}{R}\right) \exp\left(\frac{-(E_2 + \Delta H^\circ_1)}{RT}\right) \quad (6)$$

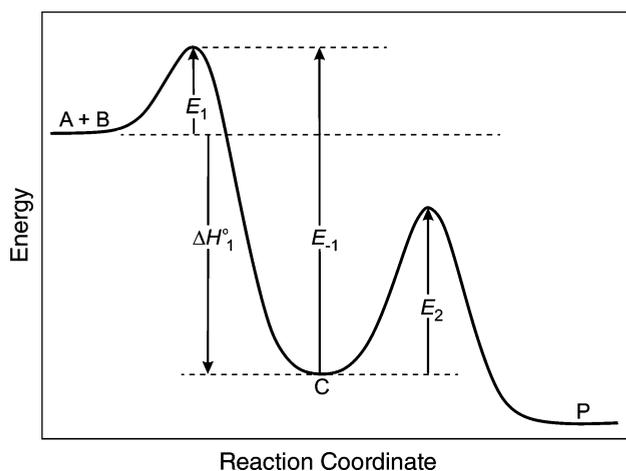
Comparing eq 6 with eq 1, it is apparent that the former is consistent with the Arrhenius law with

$$A = A_2 \exp\left(\frac{\Delta S^\circ_1}{R}\right) \quad (7a)$$

$$E_a = E_2 + \Delta H^\circ_1 \quad (7b)$$

Equations 7a and 7b reinforce the earlier point that  $A$  and  $E_a$ , respectively, provide information about entropic and enthalpic aspects of the process.<sup>9</sup> Eq 7b also shows that  $E_a$  will be negative when  $\Delta H^\circ_1 < -E_2$ . Because  $E_2$  is intrinsically positive (step 2 is elementary), this requires  $\Delta H^\circ_1 < 0$ ; so step 1 is necessarily exothermic in the forward direction *and* the maximum of the barrier for step 2 must lie at a lower energy than that of the reactants. These conditions are represented diagrammatically as a conventional energy-versus-reaction-coordinate diagram in Figure 1.

So how, physically, does this situation lead to a decreasing rate of reaction with increasing temperature? There are two contributing factors. First (and in accord with Le Chatelier’s principle), an increase in temperature shifts equilibria in favor of their endothermic direction. For the pre-equilibrium of step 1, this is the reverse direction, thus diminishing  $K_1$ , reducing the steady-state activity of C and thereby diminishing  $v_2$ . Second at higher temperatures the rate coefficients are altered in such a way that the reverse of step 1 competes (even) more effectively with step 2 for any C that does exist. This can be seen from the ratio



**Figure 1.** Reaction coordinate diagram for a reaction  $A + B \rightleftharpoons C \rightarrow P$  with an overall negative activation energy. Parameters are described in the text. The necessary conditions for a negative (overall) activation energy are that  $\Delta H^\circ_1$  is negative and that the energy of the apex of the second barrier (with activation energy  $E_2$ ) lies below the initial energy of  $A + B$  ( $E_2 < -\Delta H^\circ_1$ ).

$$\frac{v_{-1}}{v_2} = \frac{k_{-1}}{k_2} = \frac{A_{-1}}{A_2} \exp\left(\frac{E_2 - E_{-1}}{RT}\right) \quad (8)$$

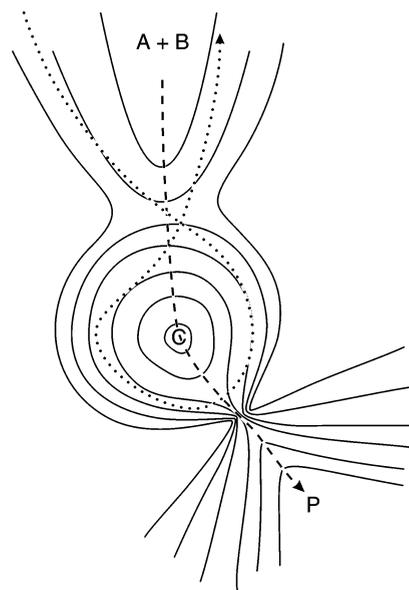
Because  $E_{-1} > E_2$ , the argument in the exponential function is negative, but it increases (becomes less negative) with increasing  $T$ , and hence  $v_{-1}/v_2$  increases. This is a specific illustration of a quite general result that the rate constants of reactions with higher activation energies increase proportionately faster with increasing temperature.

The discussion so far parallels that presented elsewhere.<sup>2,3</sup> But, as indubitably correct as it may be, it is limited to enthalpic considerations and eschews some important questions. Because  $E_{-1} > E_2$ , progression from  $C$  to  $P$  is enthalpically favored over return to reactants, which appears to run counter to the thesis of this article. Critical axioms of the model are not embedded in the enthalpic explication: that step 2 is rate determining and (hence) that pre-equilibrium is built around step 1. But how could one reasonably conclude that these conditions are commensurate with those of Figure 1? If the system has enough energy to surmount the first energy barrier, then surely it has sufficient energy to easily surmount the (necessarily lower) second barrier and proceed rapidly on to the final products?

## ENTROPIC ASPECTS

To gain a fuller understanding, it is necessary to return to the criteria stated earlier for negative  $E_a$ ; that at least one of the circumstances  $A_{-1} \gg A_2$  and  $E_2 > E_{-1}$  is met. The model just described requires  $E_{-1} > E_2$ , so the remaining explanation is that  $A_{-1} \gg A_2$ . This immediately shows that the enthalpic requirements are insufficient in their own right and must be augmented by significant entropic inferences that remain concealed in the two dimensions of a conventional reaction coordinate diagram.

A substantially more informative representation of the reaction dynamics is a contour diagram of the type illustrated by the cartoon in Figure 2; the two dimensions in the plane of the page represent the configurational space of the system whereas the contours (full lines) represent its energy. The reaction coordinate is the low-energy dashed trajectory from the reactants ( $A + B$ ) through a broad saddle (over the first



**Figure 2.** Contour plot for the reaction  $A + B \rightleftharpoons C \rightarrow P$  with an overall negative activation energy. The dimensions in the plane of the page represent the configurational space of the system, whereas the contour lines represent its energy. The dashed line corresponds to the reaction coordinate of Figure 1. The dotted line is an indicative random trajectory, which is much more likely to return to the reactants than it is to proceed to the products, even though the energy is sufficient to cross the  $C \rightarrow P$  activation barrier to reach the product state.

activation barrier) to the intermediate ( $C$ ) and then via a much narrower channel (second activation barrier) to products ( $P$ ). The critical point here is that the  $C \rightarrow P$  channel is very much narrower than the  $A + B \rightarrow C$  channel. Figure 1 represents the vertical cross section of Figure 2 through the reaction coordinate and contains none of the information about the possibility (probability) of other reaction trajectories. Because the  $C \rightarrow P$  channel is very narrow, the vast majority of reaction trajectories will extensively explore the configurational space around  $C$  before they have the opportunity to progress to  $P$ . Indeed, most trajectories (for example, the dotted line in Figure 2) are more likely to re-encounter the much broader return channel to  $A + B$  first. In terminology commonly used when describing entropy, the number of microstates in the vicinity of  $C$  that lead back to reactants is vastly greater than the number that proceed to products. Consequently, the reverse of step 1 is *entropically* very much favored over step 2, making the latter rate determining and permitting the establishment of pre-equilibrium about step 1.

It is perhaps worth noting that either or both of activation energies  $E_1$  and  $E_2$  can be zero, in which case  $E_a = \Delta H_1^\circ = -E_{-1}$ . Such so-called “barrierless” reactions occur, for example, in the case of ion–molecule reactions, which helps to explain how molecules can be formed in interstellar space at molecular densities and temperatures so low that most reactions would proceed infinitesimally slowly.<sup>10</sup> Web sites obtained in a search for “negative activation energies” (e.g., refs 11) commonly state that such reactions “are typically barrierless” and involve the “capture” of the reactant molecules in a “potential well”. Further, they typically say that the probability of capture is reduced at high temperatures “with more glancing collisions not leading to reaction as the higher momentum carries the colliding particles out of the potential well.” In terms of Figure

2, the capture process is represented by the formation of intermediate C and the potential well is the area of configurational space surrounding this intermediate. The terminology about “glancing collisions” is enticingly evocative, but is perhaps technically misleading in that it (potentially) conjures a picture in which a decrease in the reaction rate with increasing temperature arises from a higher proportion of collisions that do not lead to formation of C. A better explanation, and the one that is implied in the preceding discussion, is that, at higher temperatures, the system is able to explore the higher slopes of the potential well around C and hence is more likely to be able to exceed the barrier energy  $E_{-1} = -\Delta H_1^\circ$  when the channel back to the reactants is re-encountered.

## CONCLUSION

Reactions with negative effective activation energies are possible and do occur, even though the activation energies of the elementary steps that comprise the reaction mechanism necessarily must be non-negative. Such reactions are consequential in areas as divergent as terrestrial<sup>6</sup> and extra-terrestrial<sup>12</sup> atmospheric science, interstellar chemistry,<sup>10</sup> and enzyme catalysis.<sup>13,14</sup> But the rationalization of their temperature dependence requires considerations that extend beyond the purely enthalpic ones that are commonly presented in undergraduate text books; it is also necessary to take into account entropic factors that influence the fate of the reaction intermediate(s). The authors of this article are optimistic that discussion along the lines presented here will promulgate into future textbooks and lecturing programs at advanced levels of undergraduate chemistry, particularly in regard to the kinetics of complex reactions of atmospheric, interstellar, and biochemical relevance.

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### Notes

The authors declare no competing financial interest.

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