

Energy Barriers and Rates - Transition State Theory for Physicists

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Useful relations

$$1 \text{ cal} = 4.184 \text{ J}$$

$$1 \text{ kcal mole}^{-1} = 0.0434 \text{ eV per particle}$$

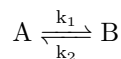
$$1 \text{ kJ mole}^{-1} = 0.0104 \text{ eV per particle}$$

$$1 \text{ eV per particle} = 23.06 \text{ kcal mole}^{-1} = 96.5 \text{ kJ mole}^{-1}$$

$$kT \text{ at } 300 \text{ K} = .0258 \text{ eV} \approx 1/40 \text{ eV}$$

1 Transition State Theory

Consider a simple two-state reaction:



Near equilibrium most reactions can be treated as “linear reactions” which means that all rates are proportional to the concentration of reactants, with no quadratic or higher order terms:

$$\begin{aligned}\dot{a}(t) &= k_1 a(t) - k_2 b(t) + \\ \dot{b}(t) &= -k_1 a(t) + k_2 b(t)\end{aligned}\tag{1}$$

Two things follow from these equations - the fact that $a(t) + b(t) \equiv C$ is constant at all times and that the equilibrium concentrations obey the detailed balance condition $-k_2 \langle b \rangle + k_1 \langle a \rangle = 0$ which allows us to define the **equilibrium constant**:

$$K \equiv \frac{\langle b \rangle}{\langle a \rangle} = \frac{k_1}{k_2}\tag{2}$$

The solution for $a(t)$ is:

$$a(t) = (a(0) - \langle a \rangle) e^{-kt} + \langle a \rangle\tag{3}$$

where

$$\begin{aligned}k &= k_1 + k_2 \\ \langle a \rangle &= \frac{a(0) + b(0)}{\frac{k_1}{k_2} - 1} = \frac{C}{K - 1}\end{aligned}\tag{4}$$

If the state B is much lower in energy than the state A , then the reaction can be considered as irreversible, and equation 3 simplifies to

$$a(t) = a(0) e^{-kt}\tag{5}$$

The goal of transition state theory is to predict the rate k of a reaction given a potential energy surface for the reaction. The potential energy surface is in general a high dimensional surface, but usually a large number of degrees of freedom (such as the orientation of molecules) can be neglected. Ideally one would like to project the potential energy surface onto a single dimension which is called the reaction coordinate. The reaction coordinate can be as simple as the distance between two molecules.

Table 1: Values of $\tau_{1/2}$ vs ΔH at $\approx 300\text{K}$. (taken from MIT OCW notes – can be confirmed using equation 7)

ΔH (kcal/mole)	ΔH (eV)	$\tau_{1/2}$
5	.22	30 ns
10	.43	2.6 s
15	.65	12 ms
20	.86	57 s
25	1.1	3.2 days
30	1.3	41 years

1.1 The Arrhenius equation

One of the accomplishments of transition state theory is the theoretical justification of the Arrhenius law, which was proposed by Svante August Arrhenius (1859-1927) in 1889:

$$k(T) = k(0)e^{-\frac{E}{k_B T}} \quad (6)$$

The factor $k(0)$ is called the prefactor and the term $e^{-\frac{E}{k_B T}}$ is an example of a Boltzmann factor.

It is easy to show that in the case of a simple exponential decay, the rate constant $k = 1/\tau$ where τ is the average time a given molecule has to wait before being reacted.

Waiting times can be approximated via the following formula:

$$\tau \approx (10^{13})e^{\frac{11604 E[\text{eV}]}{T[\text{K}]}} \quad (7)$$

For instance, a reaction with a barrier .8 eV at room temperature (300 K) will have $\tau \approx 1$ s. (As we will see below, in the harmonic approximation, the prefactor $k(0)$ is equal to the frequency of oscillation. The period of a typical bond-stretch vibration is on the order of .1 ps, thus yielding a frequency of $k(0) = 10^{13} \text{ s}^{-1}$.)

1.2 Derivation of the Arrhenius equation from T.S.T.

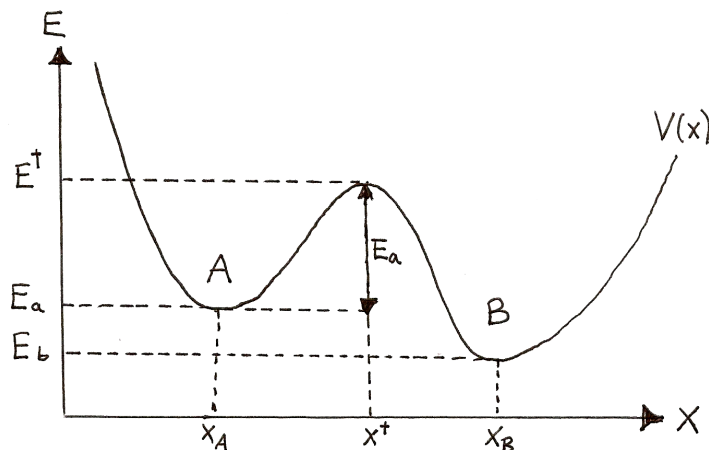


Figure 1: Transition state potential energy surface in one dimension.

There are several ways to derive the Arrhenius equation. In this section we will discuss what is (in the opinion of this author) the most elucidating derivation for physicists. Consider the 1D potential energy diagram shown in figure 1.2. The reaction coordinate x is assumed to be the distance between two molecules. From the Boltzmann distribution, we know that in equilibrium the distribution of positions x and velocities v is given by

$$P(x, v) = \frac{\exp\left[\frac{1}{kT} \left(\frac{1}{2}mv^2 + V(x)\right)\right]}{\int \int \exp\left[\frac{1}{kT} \left(\frac{1}{2}mv^2 + V(x)\right)\right] dx dv} \quad (8)$$

Transition state theory only considers particles near the top of the barrier. It is assumed that a particle moving to the right at x^\dagger will end up in state B (and likewise a particle moving to the left at x^\dagger will end up in A). This is the key assumption (and essentially the defining characteristic) of transition state theory. A way of formalizing this is as follows:

We consider particles near x^\dagger and consider their motion in a small time interval Δt . To cross the barrier in this small time interval, we require the following two conditions:

$$\begin{aligned} x^\dagger - v\Delta t &> x < x^\dagger \\ v &> 0 \end{aligned} \quad (9)$$

The probability a particle crosses the barrier in Δt we denote $P_c(\Delta t)$. However, what we are interested in is the *rate per mole of A*. That is:

$$k = \lim_{\Delta t \rightarrow 0} \frac{P_c(\Delta t)}{P_A \Delta t} \quad (10)$$

We use the Boltzmann distribution to get $P_c(\Delta t)$:

$$\begin{aligned} P_c(\Delta t) &= \frac{\int_0^\infty dv \int_{x^\dagger - v\Delta t}^{x^\dagger} dx e^{-\frac{1}{kT}(\frac{1}{2}mv^2 + V(x))}}{\int \int dv dx e^{-\frac{1}{kT}(\frac{1}{2}mv^2 + V(x))}} \\ &= \frac{\int_0^\infty dv e^{-\frac{1}{kT}(\frac{1}{2}mv^2)} \int_{x^\dagger - v\Delta t}^{x^\dagger} dx e^{-\frac{1}{kT}V(x)} + O(x - x^\dagger)}{\int \int dv dx e^{-\frac{1}{kT}(\frac{1}{2}mv^2 + V(x))}} \\ &= \frac{\int_0^\infty dv e^{-\frac{1}{kT}(\frac{1}{2}mv^2)} v \Delta t e^{-\frac{1}{kT}V(x^\dagger)}}{\int_{-\infty}^\infty dv e^{-\frac{1}{kT}(\frac{1}{2}mv^2)} \int_{-\infty}^\infty dx e^{-\frac{1}{kT}V(x)}} \\ &= \sqrt{\frac{kT}{2\pi m}} \frac{\Delta t e^{-\frac{1}{kT}V(x^\dagger)}}{\int_{-\infty}^\infty dx e^{-\frac{1}{kT}V(x)}} \end{aligned} \quad (11)$$

The probability that the particle is initially in state A is simply:

$$P_A = \frac{\int_{\Omega_A} dx \Delta t e^{-\frac{1}{kT}V(x)}}{\int_{-\infty}^\infty dx \Delta t e^{-\frac{1}{kT}V(x)}} \quad (12)$$

Combining these results into equation 10 yields:

$$k(T) = \sqrt{\frac{kT}{2\pi m}} \frac{1}{\int_{\Omega_A} \exp\left[-\frac{1}{kT}(V(x) - E_A)\right]} e^{-\frac{E_a}{kT}} \quad (13)$$

Where $E_a = E^\dagger - E_A$. The factor

$$\sqrt{\frac{kT}{2\pi m}} = \sqrt{\frac{\langle \frac{1}{2}mv^2 \rangle}{2\pi m}} = \sqrt{\frac{\langle v^2 \rangle}{2\pi}} \quad (14)$$

contains the average velocity of the particles.

We now make the **harmonic approximation**: we perform a Taylor expansion of $V(x)$ around x_A :

$$\begin{aligned} V(x) &= V(x_A) + \frac{1}{2}m\omega^2(x - x_A)^2 + O(\cancel{x - x_A})^3 \\ &\approx E_a + \frac{1}{2}m\omega^2(x - x_A)^2 \end{aligned} \quad (15)$$

We also extend the integration in the denominator of equation 13 over all of space. (This is OK since the resulting Gaussian function in the integrand will decay quickly at large distances from x_A) The resulting integral is a Gaussian integral:

$$\begin{aligned} \int_{\Omega_A} dx e^{-\frac{1}{kT}(V(x) - E_a)} &\approx \int_{-\infty}^\infty dx e^{-\frac{m\omega^2(x - x_A)^2}{kT}} \\ &= \sqrt{\frac{2kT}{m\omega^2}} \int_{-\infty}^\infty dy e^{-y^2} = \sqrt{\frac{2\pi kT}{m\omega^2}} \end{aligned} \quad (16)$$

Substituting this into 13 leads to a cancellation of factors resulting in:

$$k(T) = \frac{\omega}{2\pi} e^{-\frac{E_a}{kT}} \quad (17)$$

1.3 Thermodynamic perspective - van 't Hoff Equation

We begin with the definitions of the Gibb's and Helmholtz free energies:

$$\begin{aligned} G &= H - TS \\ H &= G + TS \end{aligned} \quad (18)$$

The differential of G is as follows:

$$dG = -SdT + VdP + \mu dN \quad (19)$$

From which it follows that $S = -\left.\frac{\partial G}{\partial T}\right|_{p,N}$ and thus

$$\begin{aligned} H &= G - T \left.\frac{\partial G}{\partial T}\right|_{p,N} \\ \frac{H}{T} &= \frac{G}{T} - \left.\frac{\partial G}{\partial T}\right|_{p,N} \end{aligned} \quad (20)$$

Now observe that

$$\begin{aligned} \frac{\partial G}{\partial T} \left(\frac{G}{T} \right) &= \frac{1}{T} \frac{\partial G}{\partial T} - \frac{G}{T^2} \\ &= \frac{1}{T} \left(\frac{\partial G}{\partial T} - \frac{G}{T} \right) \\ &= -\frac{H}{T^2} \end{aligned} \quad (21)$$

The **Gibbs-Helmholtz equation** is:

$$\left.\frac{\partial(G/T)}{\partial T}\right|_{p,N} = -\frac{H(T)}{T^2} \quad (22)$$

Now, returning to our two state equilibrium, the condition for equilibrium at constant temperature and pressure can be expressed as $\mu_A = \mu_B$. This can be seen as follows:

$$\begin{aligned} dG &= -SdT + VdP + \mu_A dN_A + \mu_B dN_B = 0 \\ \mu_A dN_A + \mu_B dN_B &= 0 \\ \mu_A dN_A - \mu_B dN_A &= 0 \\ (\mu_A - \mu_B) dN_A &= 0 \end{aligned} \quad (23)$$

In terms of the partition function of A , μ_A is

$$\mu_B = -kT \ln \left(\frac{Z_B}{N_B} \right) \quad (24)$$

The equilibrium constant is

$$K = \frac{N_B}{N_A} \quad (25)$$

The “reaction isotherm relation” is:

$$\frac{\Delta G}{T} = -k \ln K \quad (26)$$

Now using the Gibbs-Helmholtz equation, we can get the Van 't Hoff equation, first proposed by Jacobus Henricus van 't Hoff in 1884.

$$\frac{d \ln K}{dT} = \frac{\Delta H}{kT^2} \quad (27)$$

or

$$K = e^{-\frac{\Delta H}{kT}} \quad (28)$$

This is very similar to the Arrhenius equation. In fact in the same year Van 't Hoff proposed his equation, Arrhenius proposed that for a reaction with $K = k_1/k_2$, the van 't Hoff equation could be broken into two sub equations:

$$\begin{aligned}\frac{d \ln k_1}{dT} &= \frac{\Delta H_1}{kT^2} \\ \frac{d \ln k_2}{dT} &= \frac{\Delta H_2}{kT^2}\end{aligned}\tag{29}$$

This was not rigorously justified by Arrhenius, but was found to work very well.

1.4 Assumptions and limitations of T.S.T.

As you probably noticed during the derivation, transition state theory makes many assumptions. Among these are:

- The system in question is close to equilibrium.
- Only one reaction coordinate is important. The possibility of multiple pathways is ignored. The derivation can be repeated in higher dimensions with multiple pathways, but with increasing complexity. In the case of many pathways, the behavior may become non-Arrhenius.
- There is negligible barrier recrossing - ie. a molecule moving to the right at x^\ddagger is likely to wind up in B and a molecule moving to the left at x^\ddagger is likely to wind up in A . Any real system is going to spend some time in the metastable state at x^\ddagger . There will likely be oscillations around this state at a timescale τ_{mol} . The assumption of negligible barrier recrossing can be thought of as a “course graining” in time. In other words, we ignore any rapid stochastic motions of molecules around x^\ddagger and instead consider the longer time behavior. This means that TST usually fails for fast reactions, where the timescale of the reaction is the same order of magnitude as τ_{mol} .

Despite it's wide applicability, there are large classes of systems which cannot be described by TST / Arrhenius behavior. These include:

- **Systems which are far from equilibrium.** In this case, the assumption of a Boltzmann starting distribution breaks down.
- **Systems with nonlinear reaction rates.** These include systems which are far from equilibrium but also many other systems with complex behavior. In such case the rate equation is no longer linear and may contain terms quadratic or higher in the concentration.
- **Systems with very rapid reaction rates** Rapid reaction rates occur when the barrier is low and/or the temperature is high. In such case the harmonic approximation breaks down. (The probability distribution is no longer localized around the bottom of the energy well, where it can be approximated by a quadratic (harmonic) function.) Also, in the case of high rates, barrier recrossing phenomena occur on the same timescale as the reaction itself and the “course graining in time” mentioned earlier doesn't work. Also, in some reactions there is no barrier at all. Highly reactive radicals (charged species) often fall under this case. For instance, the reaction $\text{H}_3 + \text{HCN} \rightarrow \text{H}_2 + \text{H}_2\text{CN}^+$ is an extremely fast reaction which actually slows down slightly with increasing temperature. These so called “negative activation energies” are typically small, on the order of 0 to -0.08 eV.[?]
- **Isolated systems with very little energy dissipation** In isolated systems with little energy dissipation there is an obvious problem – molecules moving to the right at x^\ddagger will move into region B but then will not dissipate their kinetic energy and will move back to region A . An example of such a system is a very dilute gas with small reaction clusters. Of course, any system will lose energy via radiation, but this loss is extremely slow. Another way of stating this is that we assumed that the system is well described by a canonical ensemble and not a microcanonical.
- **Systems with light atoms (such as hydrogens).** In such systems quantum effects become important. Quantum effects tend to increase the rate for two reasons - particles lie in energy levels which are higher than the bottom of the potential energy well (ie. there is additional zero-point energy) and particles can tunnel through the barrier. These two effects

effectively lower the energy barrier. It is worth pointing out that the inclusion of quantum tunneling into the Arrhenius equation may result in the retention of the exponential form but modify the prefactor.

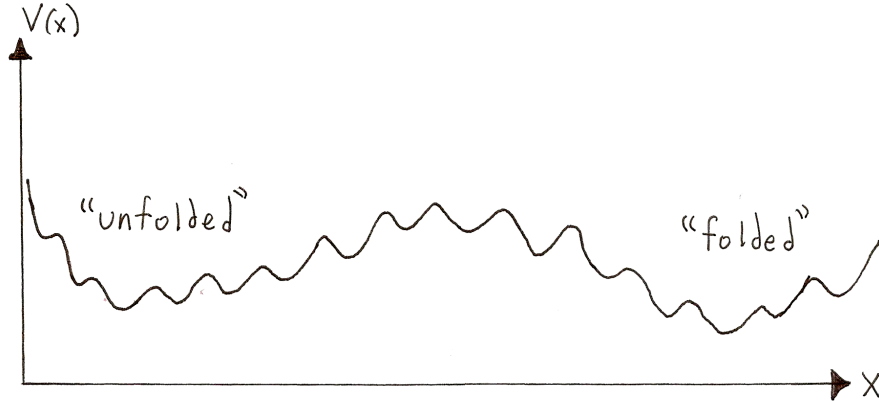


Figure 2: Hypothetical energy surface along a protein’s reaction pathway from unfolded to folded states.

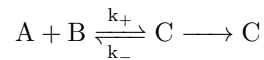
- **Systems with more complicated energy surfaces.** The archetypical example is the folding of a protein, which occurs on an energy surface in a very high-dimensional space. ($V = V[x_1, x_2, \dots, x_n]$, where n can be on the order of 1000). If we parametrize the folding trajectory using $x = x_A$ as unfolded and $x = x_B$ as folded, we will find that there are a large number of local minima on the path from unfolded to folded (figure 1.4). The movement of an ensemble of proteins in this space will be “diffusive”.

Despite having many limitations, a remarkably wide range of chemical reactions display Arrhenius behavior and can be understood in terms of T.S.T. Most chemical bonds have strengths on the order of a few eV, so the barriers are high enough and the rates slow enough that Arrhenius kinetics hold. Arrhenius kinetics also apply to many other processes, for instance, diffusion in solids. For example the diffusion constant D of carbon atoms in metal follows Arrhenius behavior between 300 – 1700 K, over which D changes by 14 orders of magnitude! This supports the interstitial model, in which the carbon atoms must jump over energy barriers from one interstitial site to another.

2 The Eyring equation

(Here ΔH is either the activation energy (NVT ensemble) or the activation enthalpy (NPT ensemble) per molecule.)

Eyring considers a somewhat more sophisticated model which considers the rate of collisions, which of course depends on temperature. He builds his model in direct analogy to a chemical reaction of the form



The linear reaction equations are:

$$\begin{aligned}\dot{a} &= k_- c^\ddagger - k_+ ab \\ \dot{b} &= \dot{a} \\ \dot{c}^\ddagger &= -k_- c^\ddagger + k_+ ab - k_2 c^\ddagger \\ \dot{c} &= k_2 c^\ddagger\end{aligned}\tag{30}$$

This is very similar to the treatment before, (if one considers $A = B$) except the intermediate state is treated as a species C^\ddagger which is known as the **activated complex**. This makes a lot of sense in certain cases, which correspond to potential energy surfaces with a large plateau region.

As was mentioned, the mean velocity of an ideal gas is $\langle v \rangle = (kT/2\pi m)^{1/2}$. Using this, Bauer defines the time it takes for an activated complex to cross the energy barrier as $t^* = \delta/\langle v \rangle = 1/k_-$ where δ is the “width” of the barrier. This width is not properly defined here at all, but luckily one finds that it cancels out in the final expression. At equilibrium the rate k_+ will be

$$k = \frac{c^\ddagger}{abk_-} = \frac{c^\ddagger (kt/2\pi m)^{1/2}}{ab\delta} \quad (31)$$

Thermodynamic reasoning allows us to say that

$$\begin{aligned} \frac{c^\ddagger}{abk_-} &= \frac{\exp\left(\frac{-G^\ddagger}{kT}\right)}{\exp\left(\frac{-G_A}{kT}\right) \exp\left(\frac{-G_B}{kT}\right)} \\ &= \exp\left(\frac{(G_A + G_B) - G^\ddagger}{kT}\right) \end{aligned} \quad (32)$$

Now he separates out the energy $(2\pi mkT)^{1/2}\delta/h$:

$$\frac{c_*}{c_{ACB}} = \frac{(2\pi mkT)^{1/2}\delta}{h} \exp\left(\frac{(G_A + G_B) - G'}{kT}\right) \quad (33)$$

Substituting this into 31 we get

$$k = \frac{kT}{h} \exp\left(-\frac{\Delta G}{kT}\right) \quad (34)$$

Since $G = H - ST$ we get the **Eyring equation**:

$$k = \frac{kT}{h} \exp\left(\frac{\Delta S}{k}\right) \exp\left(-\frac{\Delta H}{kT}\right) \quad (35)$$

We see that if we treat the term with the entropy as a constant, this is similar to the Arrhenius law except with a factor of T out front. Note that treating ΔS as constant and independent of temperature is an approximation, but within a limited temperature range can be a reasonable one. The frequency factor is replaced with $\frac{kT}{h}$ which again has units of frequency and implies that this frequency corresponds to a mode with energy equal to the thermal energy kT .

2.1 The collision theory

The collision theory is another way to derive Arrhenius behavior. It is considered to be a separate theory from TST, but is very similar. It simply assumes that in a reaction $A + B \longrightarrow C$ between two molecules of species A and B will occur only once they collide with sufficient energy. Thus, the rate of the reaction is:

$$\text{Rate} = \frac{\text{Number of effective collisions}}{\text{mole / sec}} = \left\{ \frac{\text{Total number of collisions}}{\text{mole / sec}} \right\} \times \left\{ \frac{\text{Fraction of collisions with sufficient energy}}{\text{mole / sec}} \right\} \times \left\{ \frac{\text{Fraction of collisions that have proper orientation}}{\text{mole / sec}} \right\} \quad (36)$$

Kinetics tells us that the collision frequency for an ideal dimolecular gas is

$$\text{Collision freq.} = f = \pi \left(\frac{r_A + r_B}{2} \right)^2 \sqrt{\frac{8kT}{\pi\mu}} n_A n_B \quad (37)$$

where μ is the reduced mass ($\mu^{-1} = m_A^{-1} + m_B^{-1}$) of the system and r_A and r_B are the effective radii of molecules A and B .

The fraction of molecules with sufficient energy is simply given by the proper Boltzmann factor. We will not try to evaluate the orientation factor here but will simply assume it is a temperature independent factor p (for atomic species p can be considered equal to one).

The resulting equation is :

$$k = pf \exp\left(-\frac{E_{\text{act}}}{kT}\right) \quad (38)$$

2.2 Summary

In summary, there are three commonly used variations of the Arrhenius law which differ in the prefactor. The T.S.T. derivation yielded a factor of $T^{1/2}$ which is the same prefactor obtained in a derivation by Bauer. Bauer's derivation considers rotational relaxation and is attempt to explain the observed temperature dependence of the Debye relaxation time $\tau_D = 1/k_D$ which follows the Arrhenius law for many substances. Bauer's derivation proceeds similar to Eyring's but instead of considering a one dimensional PE surface, he more explicitly considers a rotation in 3D space from one region to another across an energy barrier separating the two regions. These three models can be summarized as follows:

$$k(T) = AT^n \exp\left(-\frac{\Delta H}{kT}\right) \quad \text{where} \quad \begin{cases} n = 0 & (\text{Arrhenius / TST with harmonic approx.}) \\ n = 1 & (\text{Eyring}) \\ n = 1/2 & (\text{TST / Bauer / collision theory}) \end{cases} \quad (39)$$

In practice, the difference between these three models can be difficult to distinguish experimentally unless one considers a very broad range of temperatures.

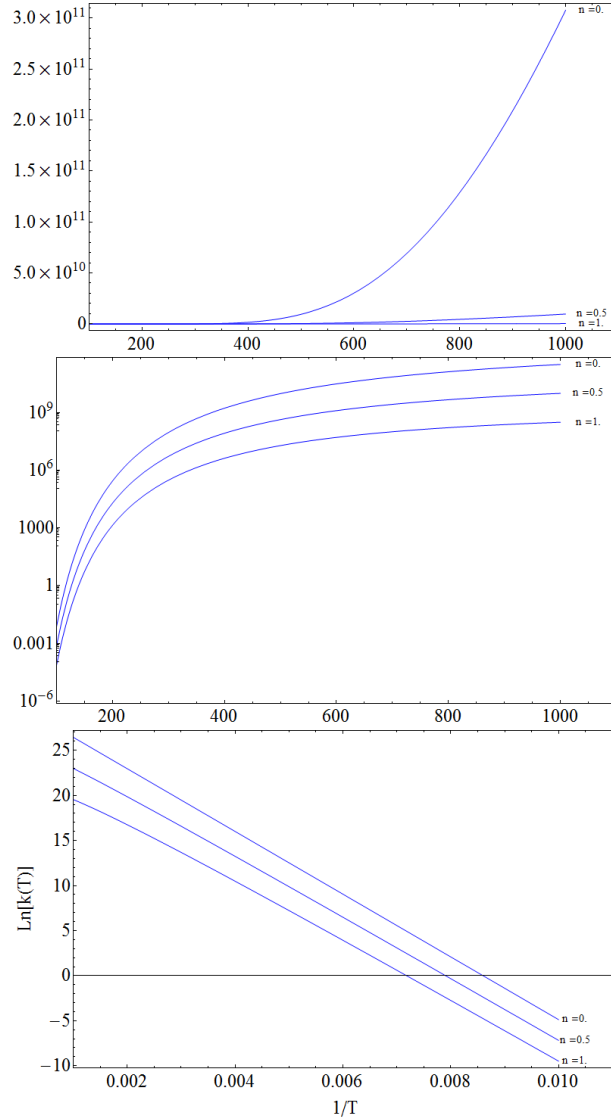


Figure 3: Plots of $k(T)$ for the three equations listed in 39.

Figure 2.2 illustrates this by plotting $k(T)$ for the three equations in three different ways. The first plot is a simple linear plot, which presents a dramatic divergence to the eye. The second plot

is a logarithmic plot which emphasizes the common exponential nature of the three expressions. The third plot is called an Arrhenius plot and is a very popular way of plotting this type of data (the slope of this plot gives the activation energy).

References