SciFun

Chemical Kinetics – 5

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Exercise: the mistery of Rapa Nui

Rapa Nui (Easter Island) is one of the most remote inhabited places on Earth, located 3,700 km from South America and over 2,000 km from the nearest inhabited island. The island is famous for its nearly 1,000 monumental stone statues called moai, carved by the Polynesian settlers who arrived around 1200.

For decades, the popular narrative (made famous by Jared Diamond's book "Collapse") suggested that the Rapa Nui civilisation experienced a catastrophic collapse around 1600 CE due to deforestation and resource depletion, before the first arrival of Europeans, in 1722. Your mission is to prove or disprove this theory.
In order to do that, you joined an archaeological team excavating at Ahu Nau Nau (a ceremonial platform on Rapa Nui) and collected several samples for carbon-14 dating. These are the results:

Sample	Description	% ^{14}C remaining	Context
A	Charcoal from earliest settlement layer	90.5%	First colonisation
B	Wood fragment from moai transport ramp	93.2%	Statue building
C	Bone fragment from burial under ahu	95.8%	Late ceremonial use
D	Seed from red pigment pit	94.5%	Pigment production

What happened to the Rapa Nui civilisation?

Exercise: the mistery of Rapa Nui

First, we calculate the carbon-14 decay reaction constant:

$$t_{1/2} = \frac{\ln 2}{k}$$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{5730 \text{ yr}} = 1.21 \times 10^{-4} \text{ yr}^{-1}$$

And then, we calculate the age of the samples

$$[\mathrm{A}] = [\mathrm{A}]_0 \, e^{-kt}$$

$$\Rightarrow \quad \ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt \quad \Rightarrow \quad t_{\text{samples}} = \frac{\ln \frac{[\mathrm{A}]_0}{\mathrm{A}}}{k} = \frac{\ln(\% \ {}^{14}\mathrm{C} \text{ remaining})}{k}$$

$$t_A = \frac{\ln(100/90.5)}{1.21 \times 10^{-4} \text{ yr}^{-1}} = \frac{0.0998}{1.21 \times 10^{-4} \text{ yr}^{-1}} = 825 \text{ yr}$$

$$t_B = \frac{\ln(100/93.2)}{1.21 \times 10^{-4} \text{ yr}^{-1}} = \frac{0.0704}{1.21 \times 10^{-4} \text{ yr}^{-1}} = 582 \text{ yr}$$

$$t_C = \frac{\ln(100/95.8)}{1.21 \times 10^{-4} \text{ yr}^{-1}} = \frac{0.0431}{1.21 \times 10^{-4} \text{ yr}^{-1}} = 354 \text{ yr}$$

$$t_D = \frac{\ln(100/94.5)}{1.21 \times 10^{-4} \text{ yr}^{-1}} = \frac{0.0564}{1.21 \times 10^{-4} \text{ yr}^{-1}} = 467 \text{ yr}$$

Exercise: the mistery of Rapa Nui

Sample	Description	% ^{14}C remaining	Context	Age	Year	Interpretation
A	Charcoal from earliest settlement layer	90.5%	First colonisation	825 yr	**~1201**	First settlement
B	Wood fragment from moai transport ramp	93.2%	Statue building	582 yr	**~1444**	Peak moai building
C	Bone fragment from burial under ahu	95.8%	Late ceremonial use	354 yr	**~1672**	After "collapse"
D	Seed from red pigment pit	94.5%	Pigment production	467 yr	**~1559**	Pigment production

Sample A dates to ~1201, consistent with current archaeological consensus that Polynesian colonisation occurred around 1200. Sample C dates to ~1672, showing that ceremonial activities continued 70 years after the supposed collapse. The dates show continuous cultural activity from settlement (~1201) through European contact (1722). There is no evidence of a sudden collapse in the archaeological record.

Reaction mechanisms

So far, we have obtained all our information about the reaction from experiments. From these measurements, we can determine the reaction orders and the rate constant. However, this approach does not tell us the individual molecular steps the reaction actually follows. These fundamental steps, which describe what is happening at the molecular level, are known as the reaction mechanism. A mechanism is proposed based on theoretical reasoning (as a hypothesis) and must then be tested and validated through lots of experiments.

Overall reaction

$$2\ NO_2(g) + F_2(g) \rightarrow 2\ NO_2F(g)$$

Elementary Steps

1. $NO_2 + F_2 \rightarrow NO_2F + F$
2. $NO_2 + F \rightarrow NO_2F$

📖 Reaction mechanism: The sequence of elementary steps that connect reactants and products.
Reaction intermediates: Molecules or chemical species that form temporarily during the reaction and disappear before the final products are formed.

Elementary reactions

Molecularity	Elementary Reaction	Rate law
Unimolecular	A → products	$r = k\,[A]$
Bimolecular	A + A → products	$r = k\,[A]^2$
Bimolecular	A + B → products	$r = k\,[A][B]$
Termolecular	A + A + A → products	$r = k\,[A]^3$
Termolecular	A + A + B → products	$r = k\,[A]^2[B]$
Termolecular	A + B + C → products	$r = k\,[A][B][C]$

If a reaction is elementary, its rate law is based directly on its molecularity

Molecularity: The number of molecules that participate as reactants in an elementary reaction
Elementary reaction: Reactions that occur in a single event or step

Rate-determining step

Overall reaction

$$2\ NO_2(g) + F_2(g) \rightarrow 2\ NO_2F(g)$$

Elementary Steps

Slow	1.	$NO_2 + F_2 \rightarrow NO_2F + F$	*Bimolecular: two molecules collide*
Fast	2.	$NO_2 + F \rightarrow NO_2F$	*Bimolecular: uses the F atom produced in step 1*

The rate-determining step is the slowest step in a reaction mechanism. It acts as a "bottleneck" that limits the overall reaction rate.

Rate-determining step

Overall reaction

Elementary Steps

Sl

Fo *ced in step 1*

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$$r = k[NO_2][F_2]$$

This is our proposed reaction mechanism. If we carry out the experiment and find that the reaction is first order with respect to NO_2 and first order with respect to F_2, then all we can conclude is that the rate law predicted by the mechanism is consistent with the experimental results.

Exercise

The decomposition of ozone in the atmosphere occurs according to the following overall reaction:

$$2\,O_3 \rightarrow 3\,O_2$$

Scientists have proposed the following two-step mechanism:

Step 1: $O_3 \rightarrow O_2 + O$ (fast)
Step 2: $O_3 + O \rightarrow 2\,O_2$ (slow)

a) Identify the intermediate in this mechanism
b) Which step is the rate-determining step?
c) What is the molecularity of each step?

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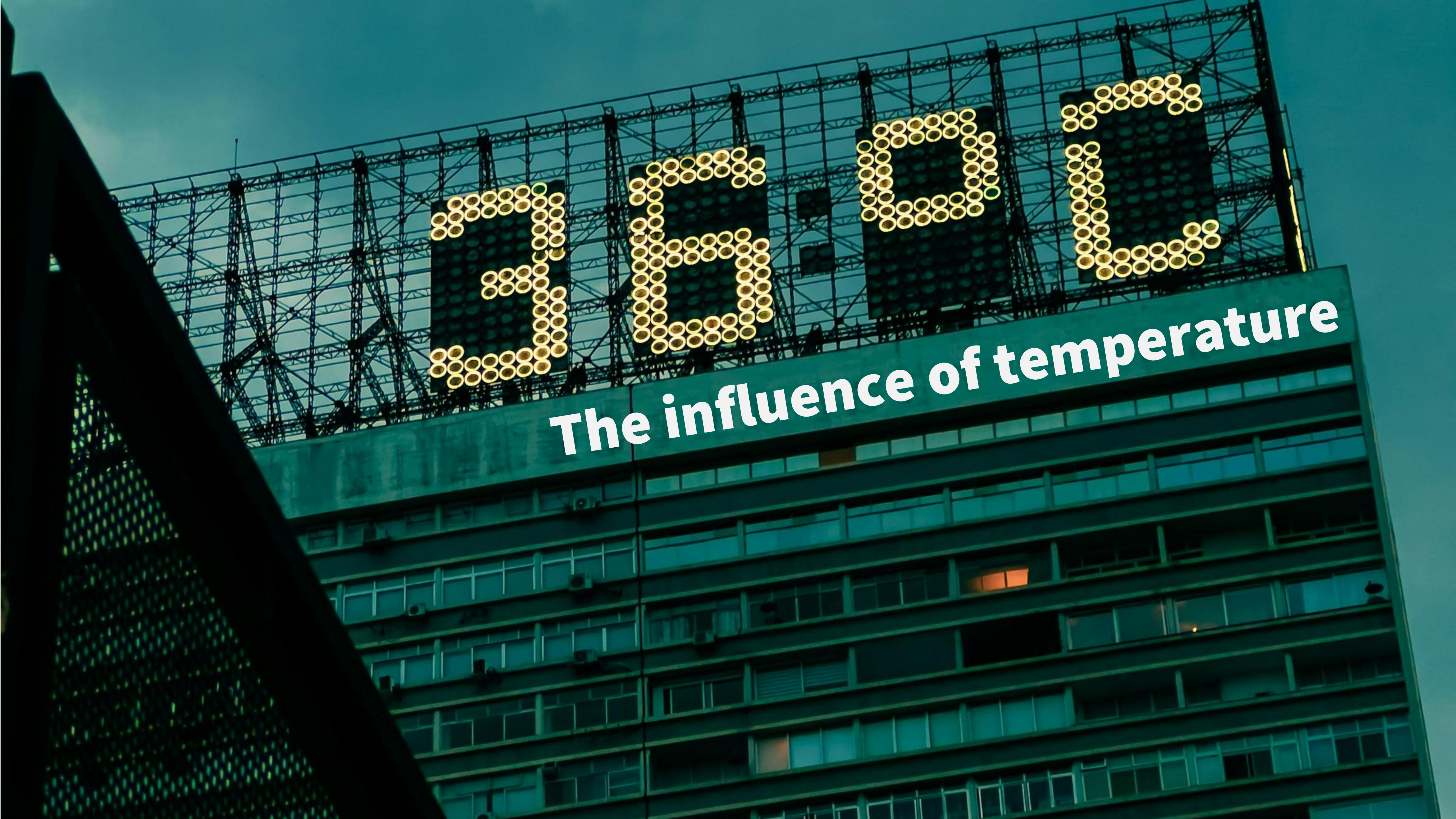
Step 2: $O_3 + O \rightarrow 2\ O_2$ (slow)

a) Identify the intermediate in this mechanism
   The intermediate in this mechanism is the atomic oxygen.
b) Which step is the rate-determining step?
   Step 2
c) What is the molecularity of each step?
   Step 1: Unimolecular reaction
   Step 2: Bimolecular reaction


36°C
The influence of temperature

Temperature Matters More Than You Think

Fluorine

$$F_2 + H_2 \xrightarrow{\cdot} 2\ HF$$

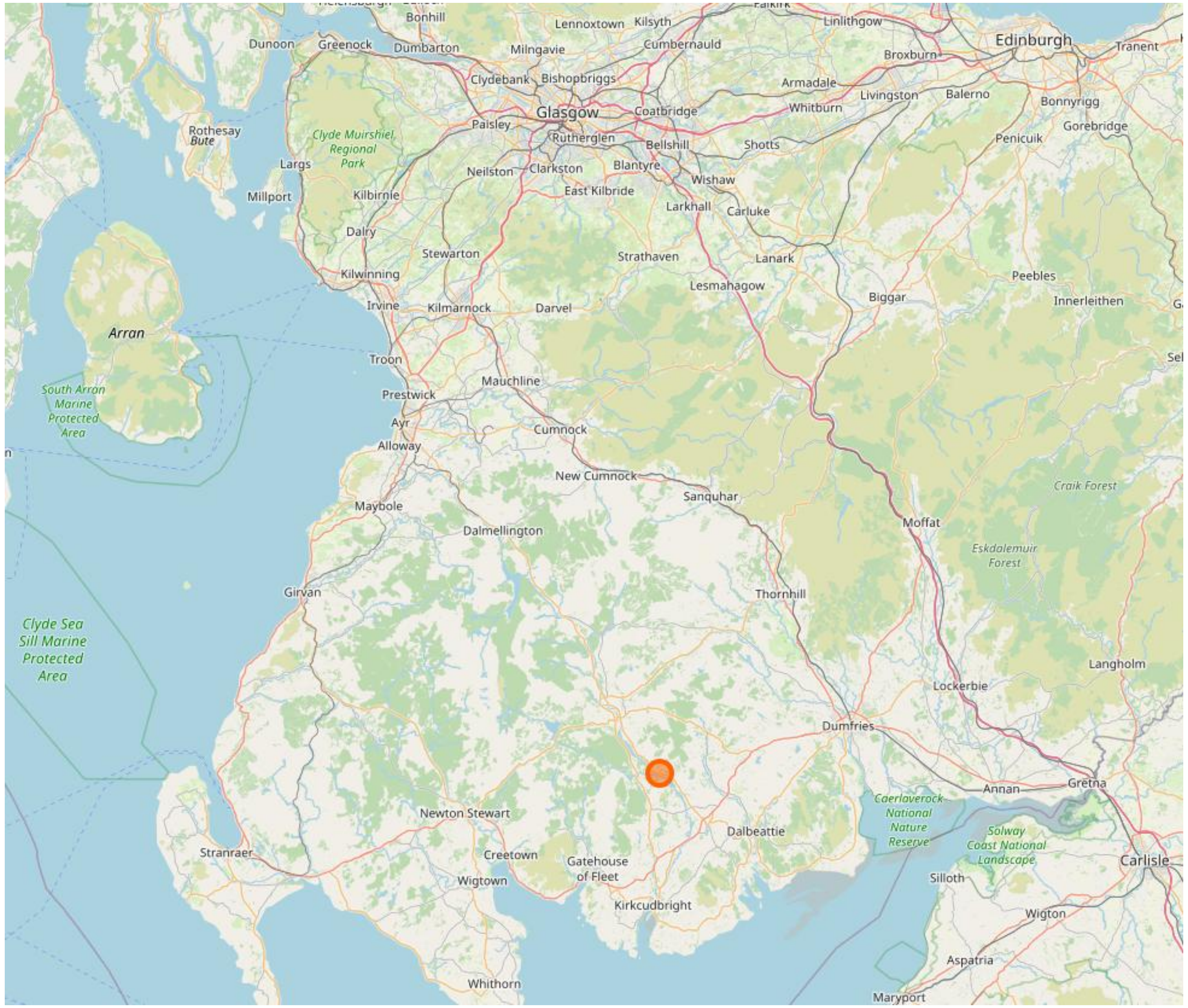
Fast, almost explosive

$$I_2 + H_2 \xrightarrow{\cdot} 2\ HI$$

Veeeeery slow

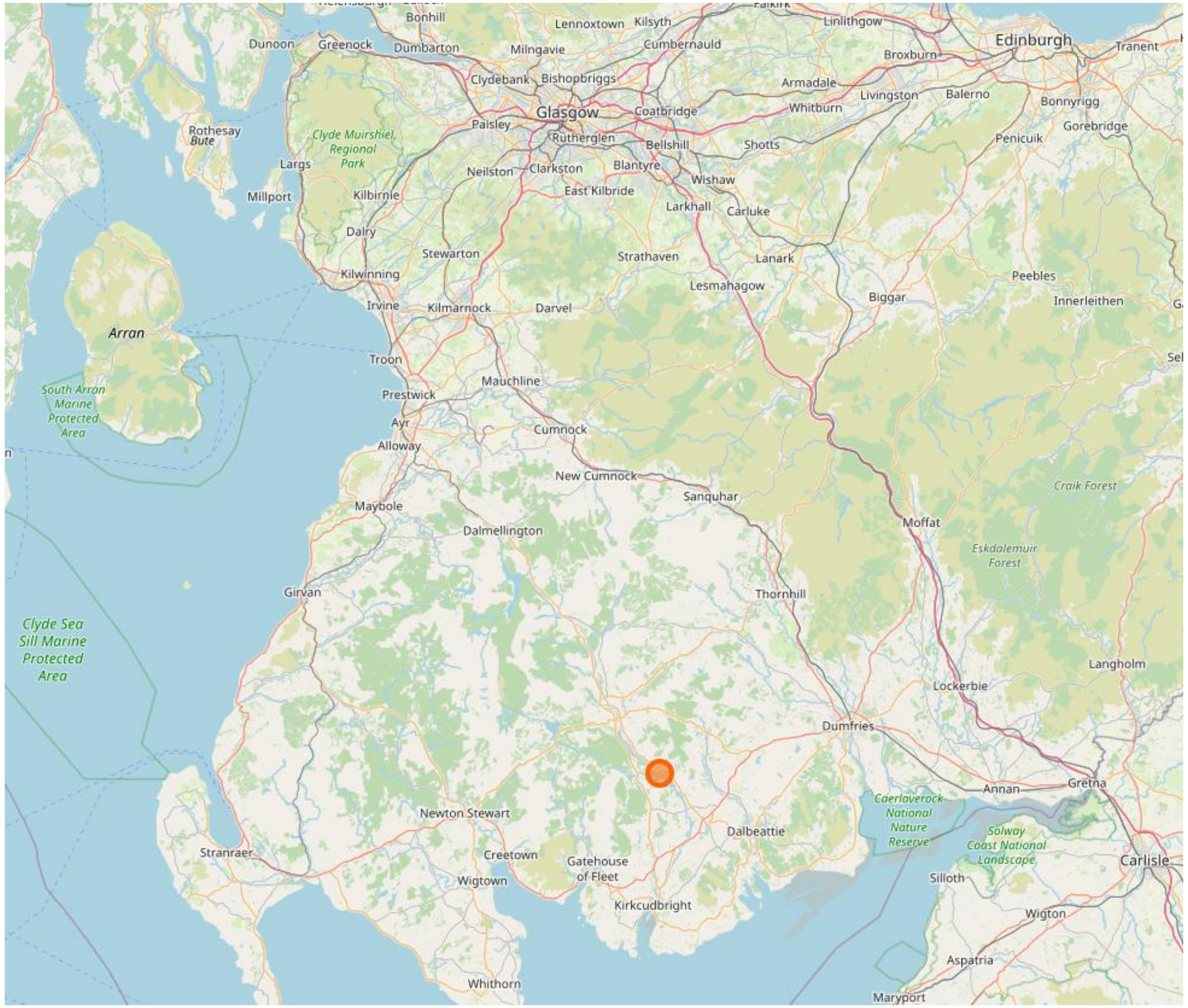
Iodine

Statistical mechanics

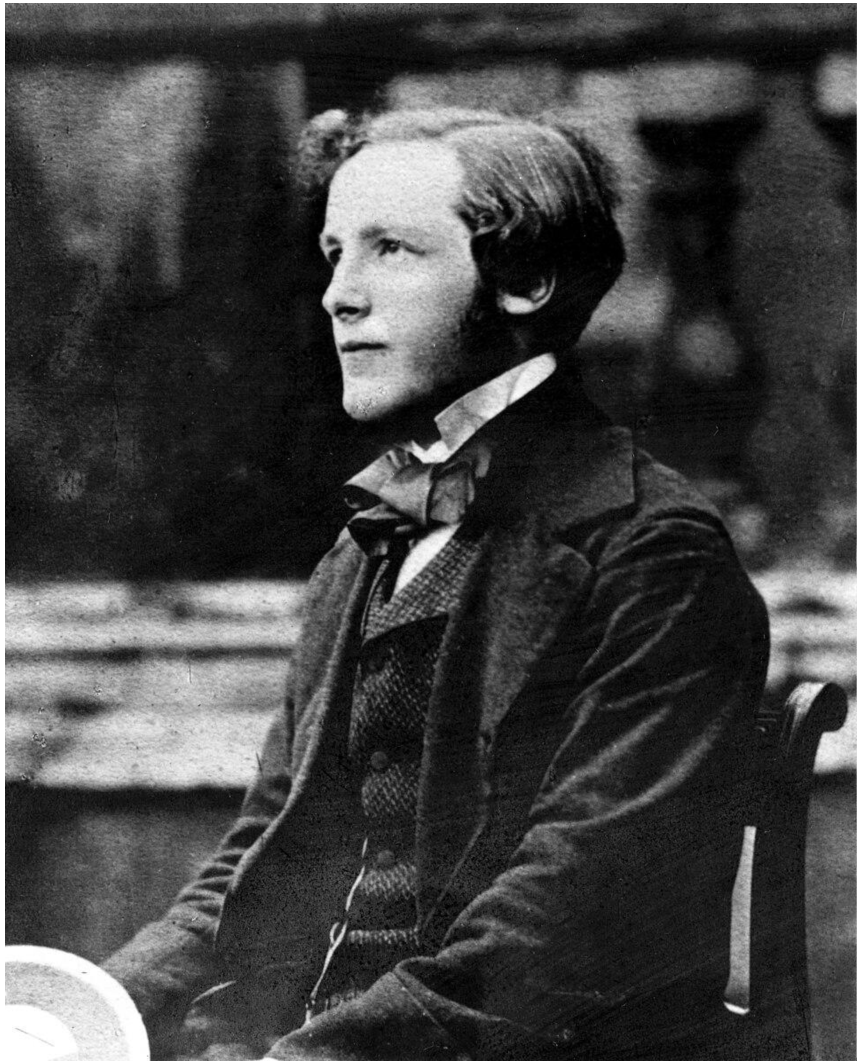


Parton Parish Church

Statistical mechanics

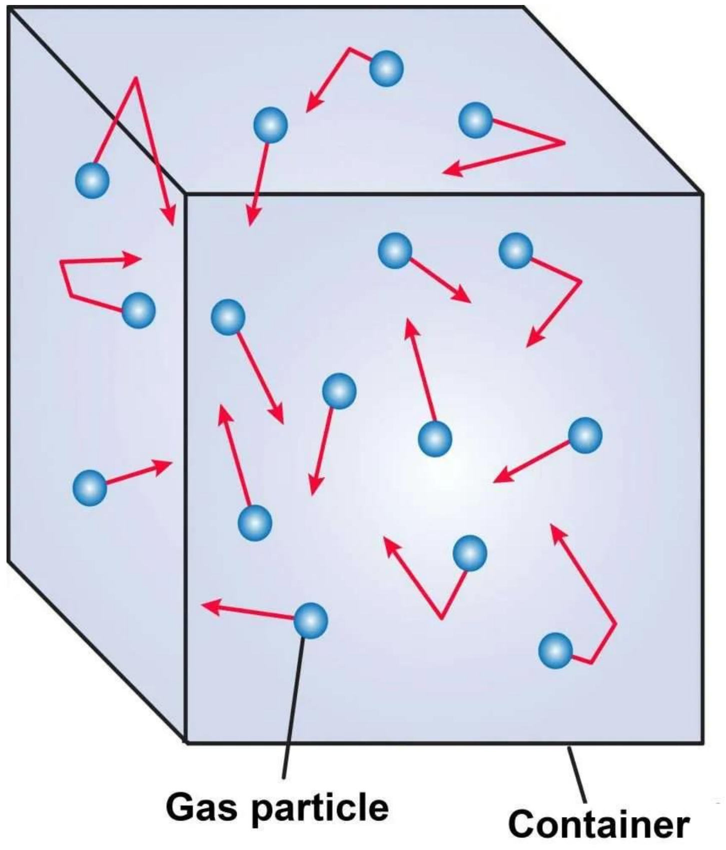


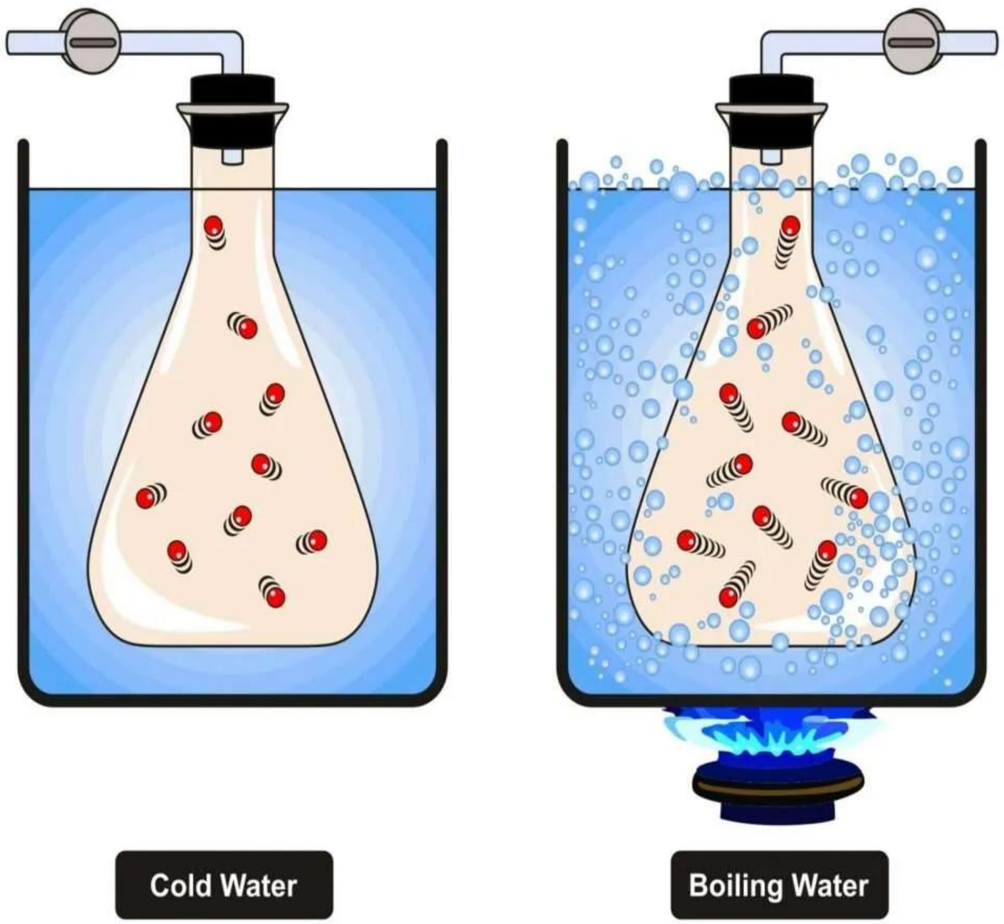
Parton Parish Church



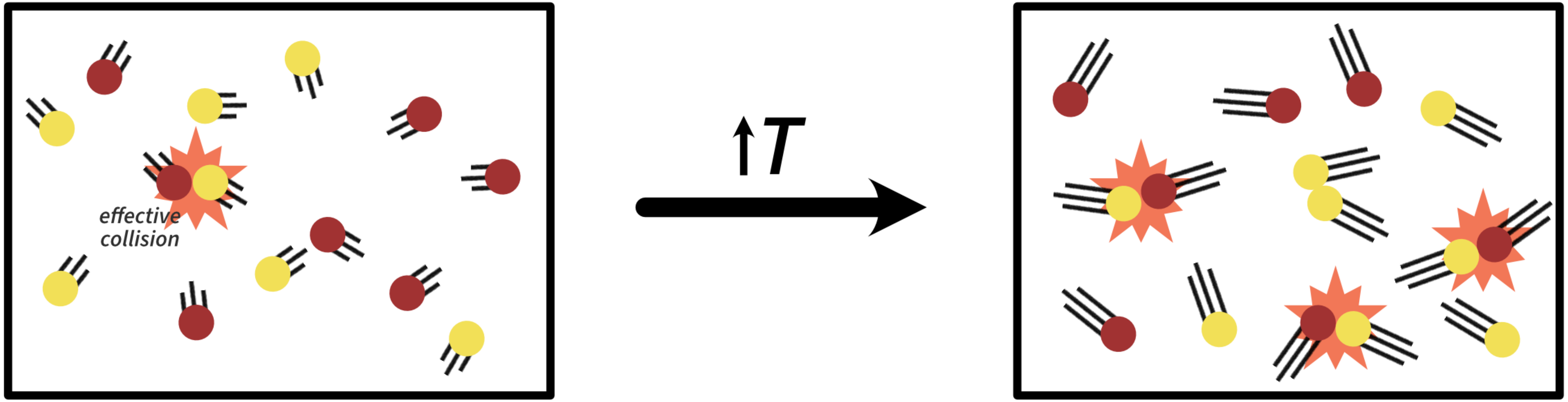
James Clerk Maxwell

Statistical mechanics





Collision theory of chemical reactions



The problem with collision theory

$$F_2 + H_2 \longrightarrow 2\ HF \qquad r = k[F_2][H_2]$$

Temperature / °C	Temperature / K	k / $M^{-1}\ s^{-1}$
0	273	3.1×10^9
25	298	6.3×10^9
35	308	7.7×10^9
50	323	9.7×10^9
75	348	1.4×10^{10}
100	373	1.9×10^{10}

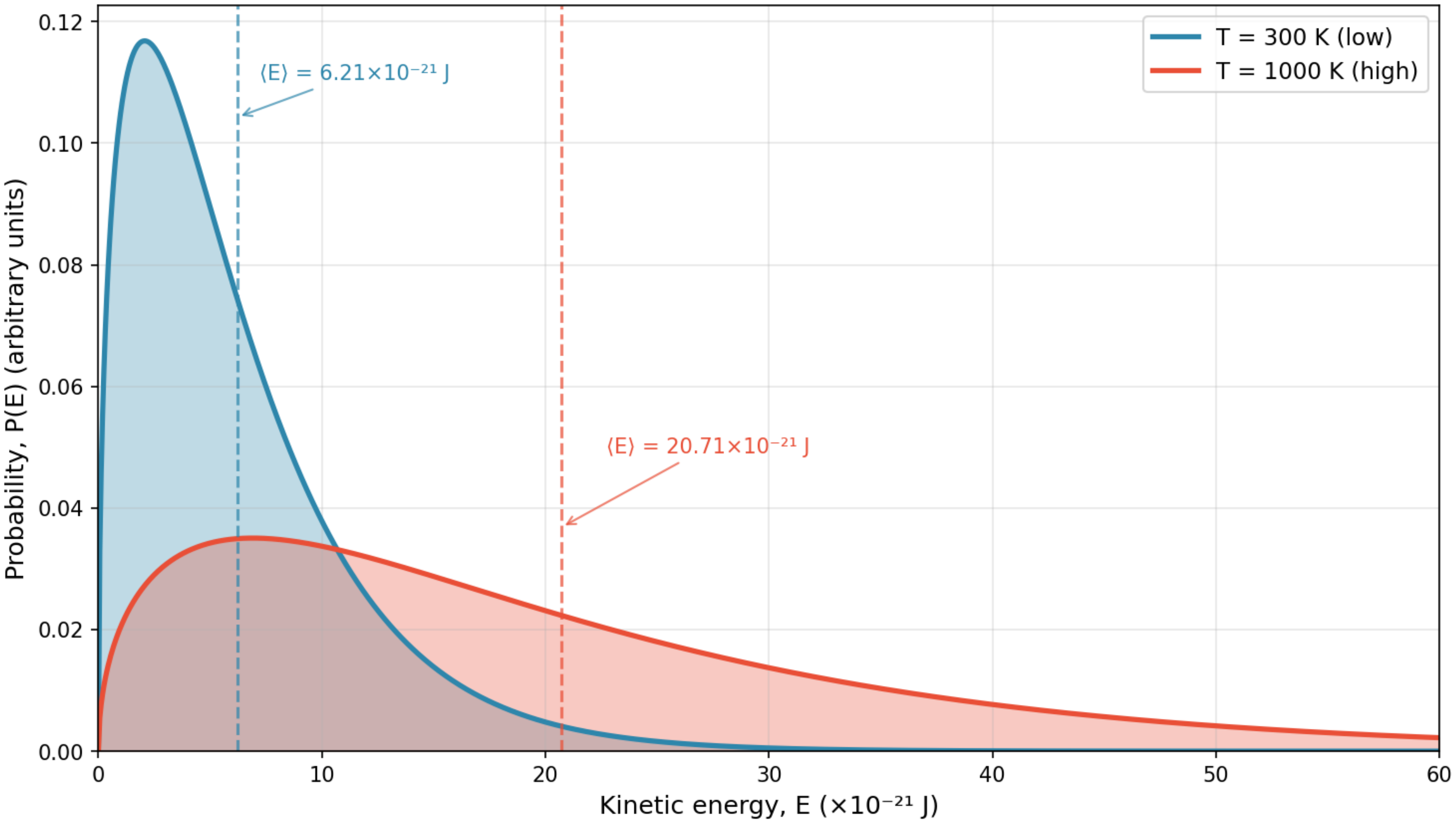
+22%

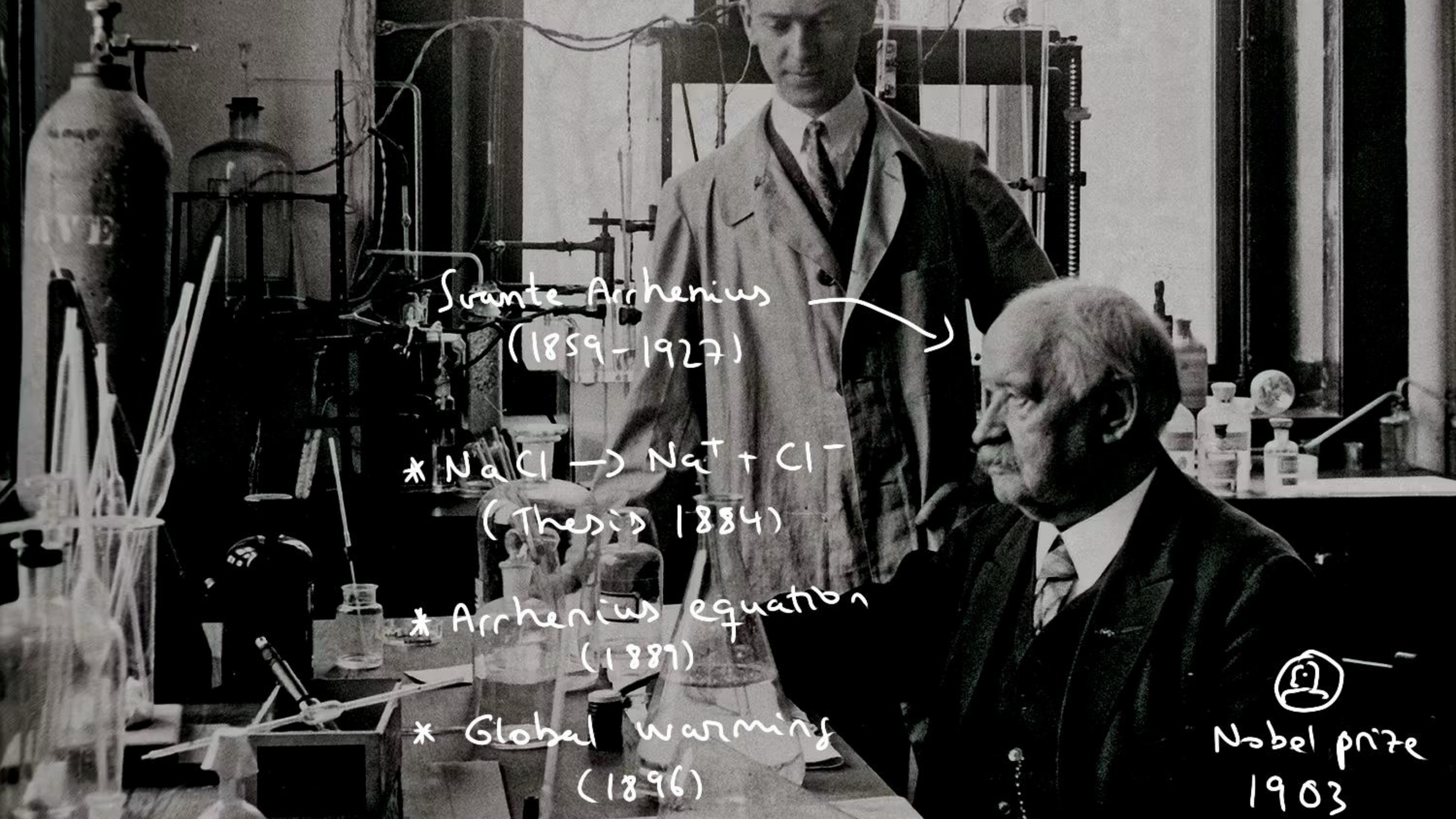
But according to the collision theory...

$$\bar{v} \propto \sqrt{T}$$

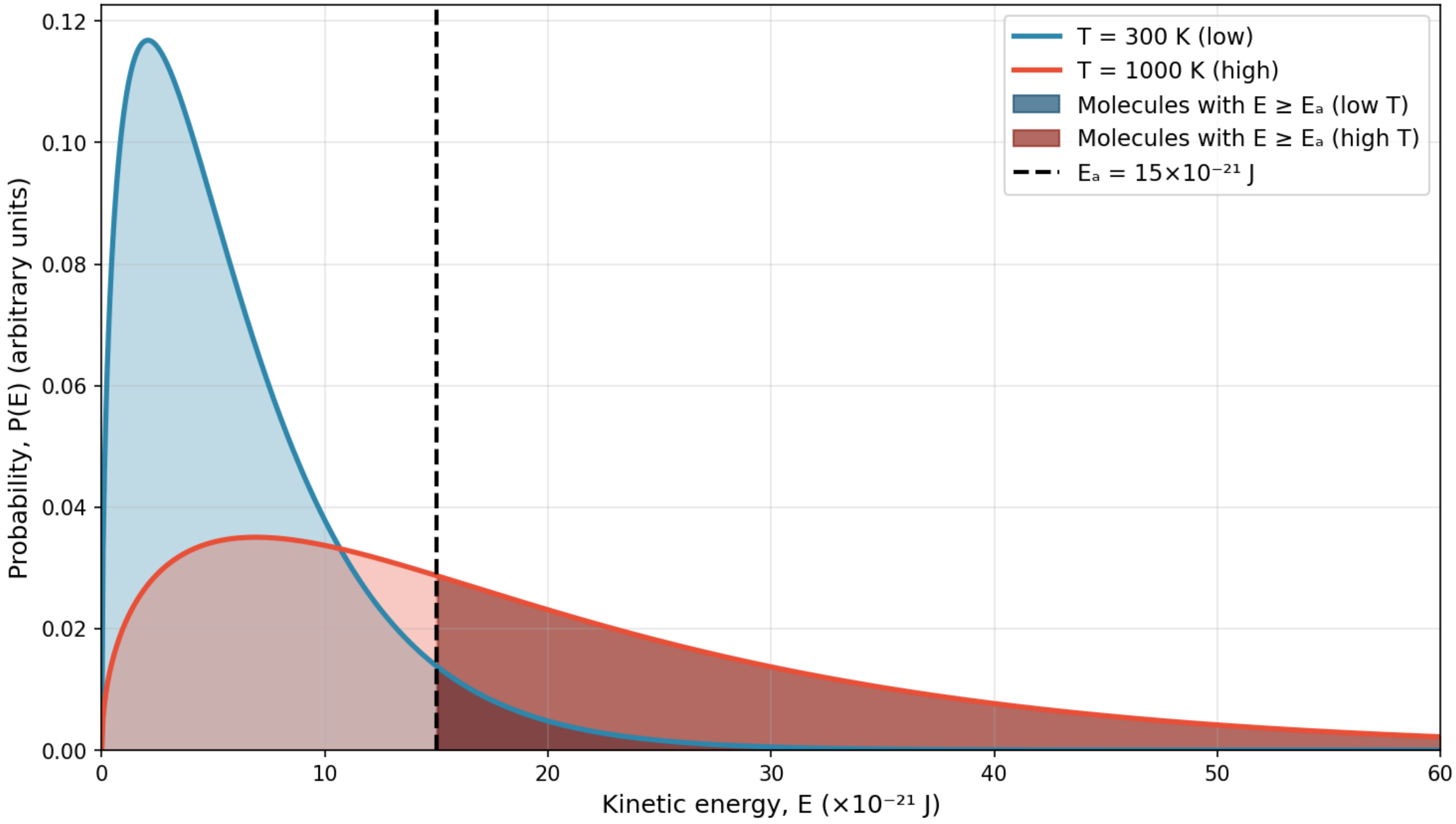
$$\frac{\sqrt{308}}{\sqrt{298}} = 1.016 \longleftarrow \textbf{+1.6\%}$$

Distribution of kinetic energies




Svante Arrhenius
(1859-1927)
* NaCl → Na+ + Cl−
(Thesis 1884)
* Arrhenius equation
(1889)
* Global warming
(1896)
Nobel prize
1903

Svante's idea: Activation Energy



Arrhenius equation

Frequency factor
(The same units as *k*)

Activation energy
(J mol^{-1})

$$k = Ae^{-\frac{E_a}{RT}}$$

Rate constant
(Units depend on order)

Average energy of the system
(R = 8.314 J mol^{-1} K^{-1})

This is why the rate constant *k* increases with temperature: it's not that collisions become more frequent (that's captured by the frequency factor *A*), but rather that a larger proportion of those collisions are effective.

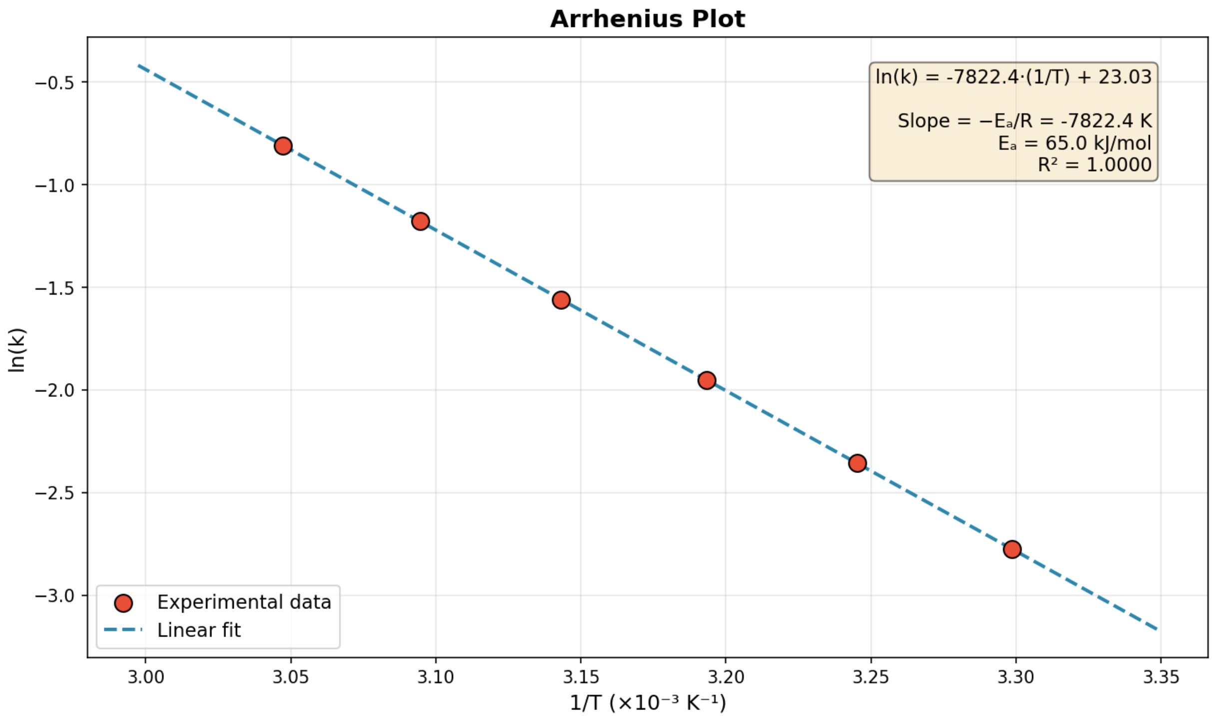
Arrhenius equation

$$k = Ae^{-\frac{E_a}{RT}}$$

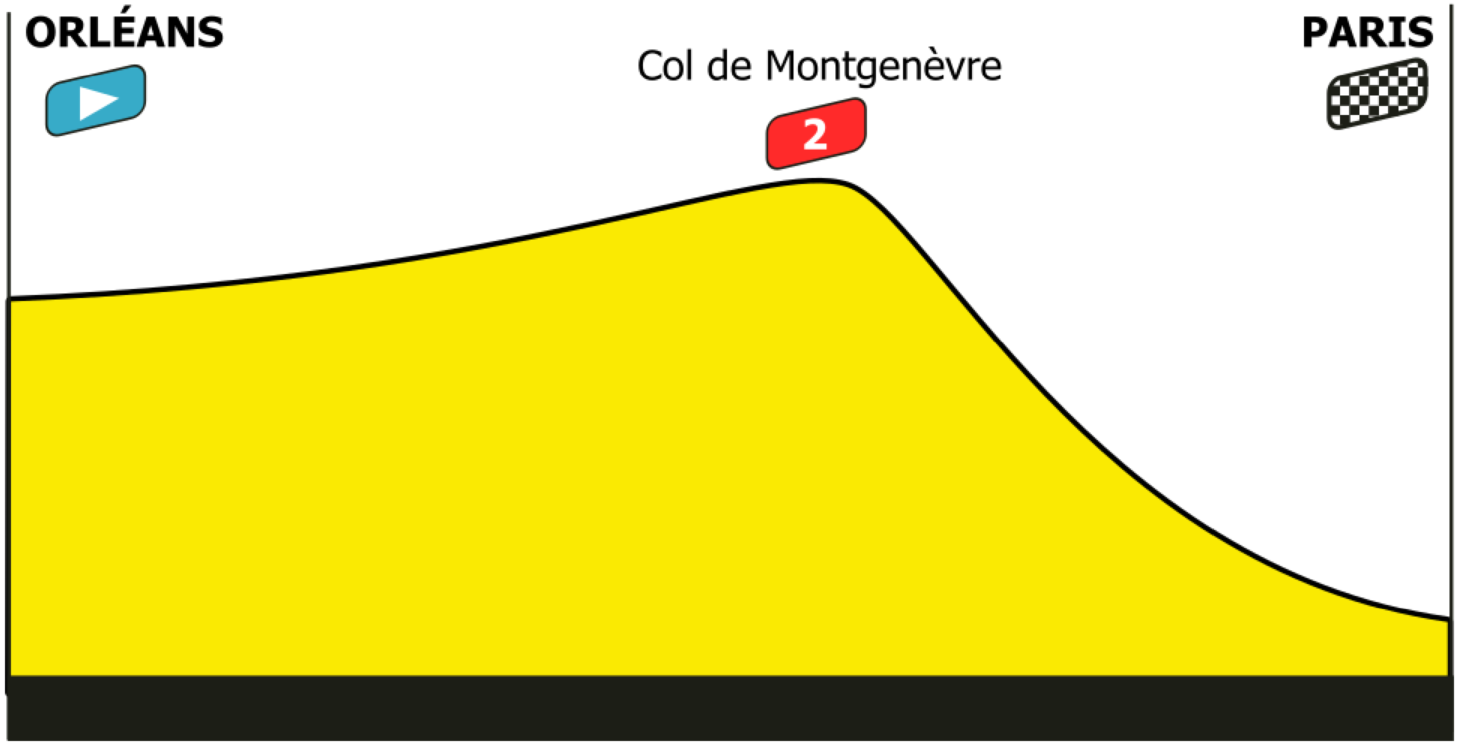
$$\ln k = \ln A - \frac{E_a}{R}\frac{1}{T}$$

$(y = a + b\,x)$

Temperature (ºC)	k (s-1)
30	0.0623
35	0.0948
40	0.142
45	0.21
50	0.308
55	0.445

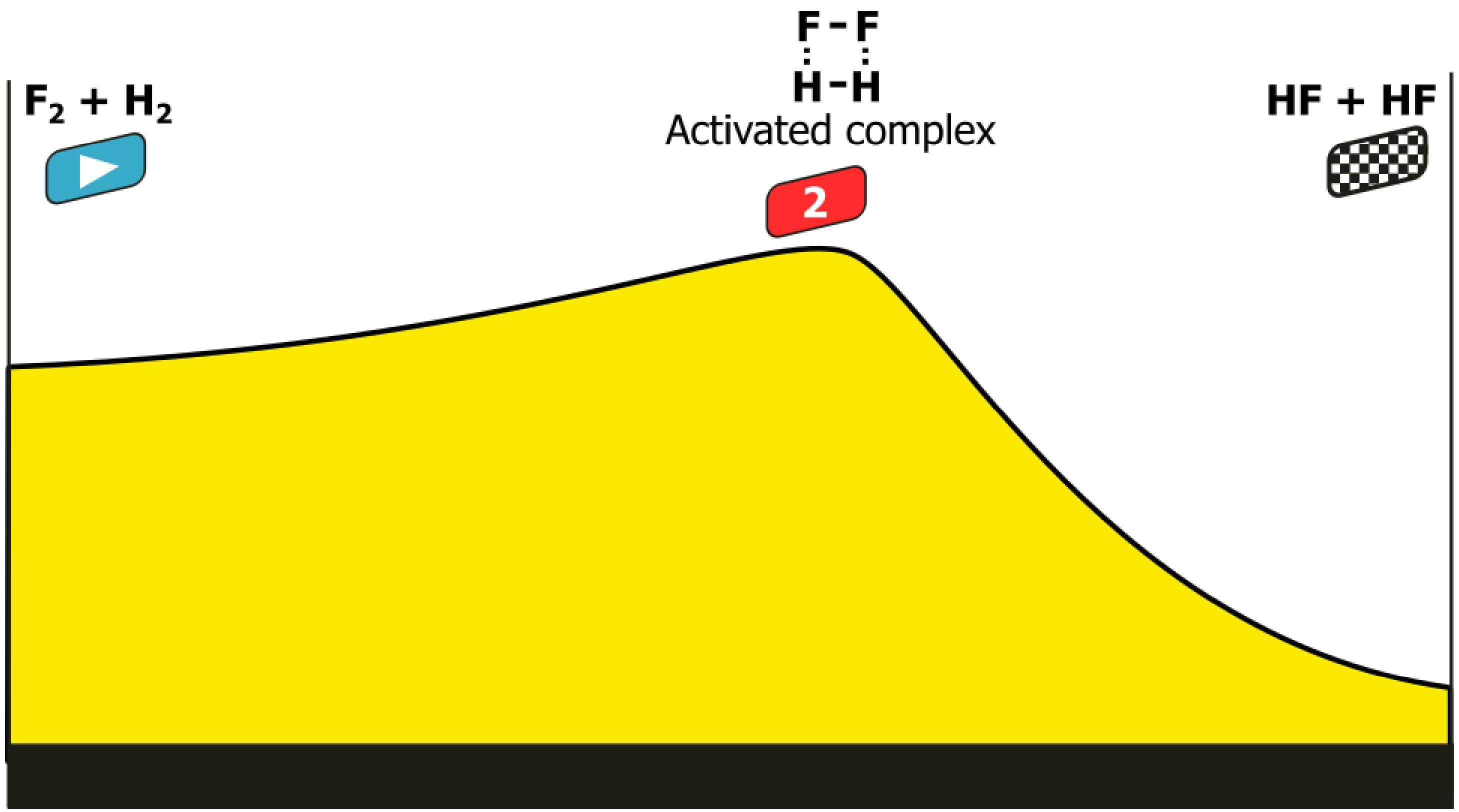


Understanding the activation energy



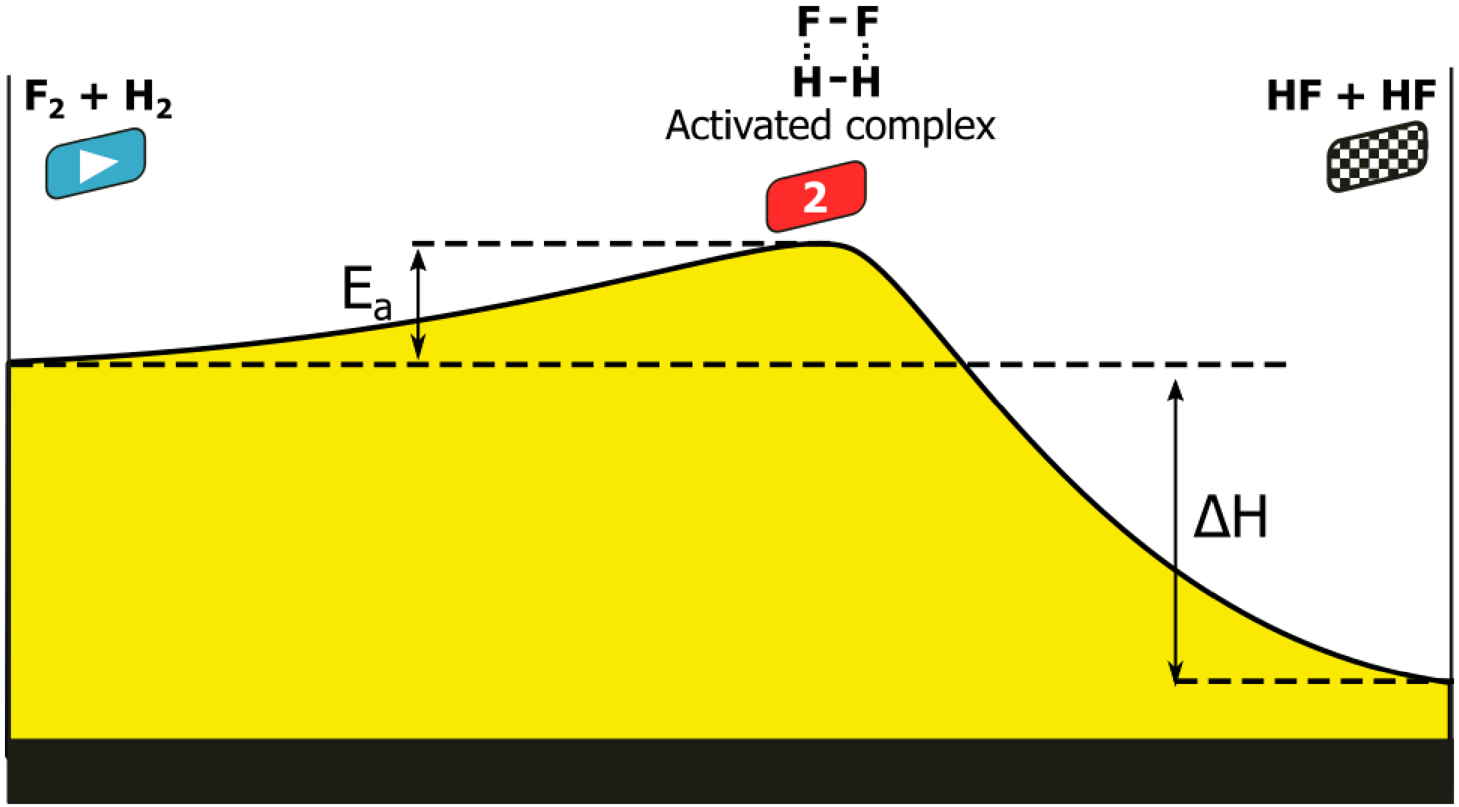
Elevation Profile and Potential Energy of a Tour of France Stage

Understanding the activation energy



Reaction Coordinate Diagram for HF Formation

Understanding the activation energy



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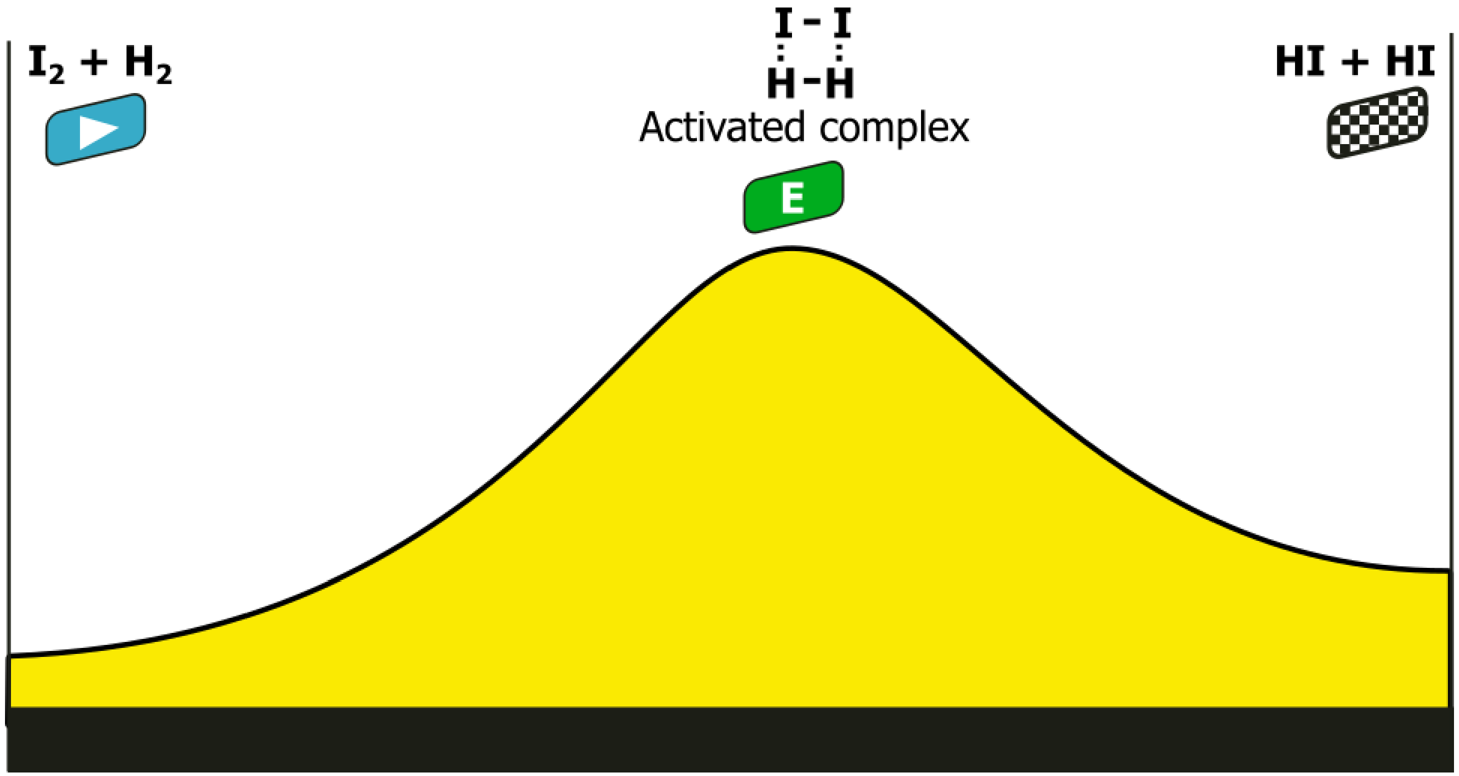
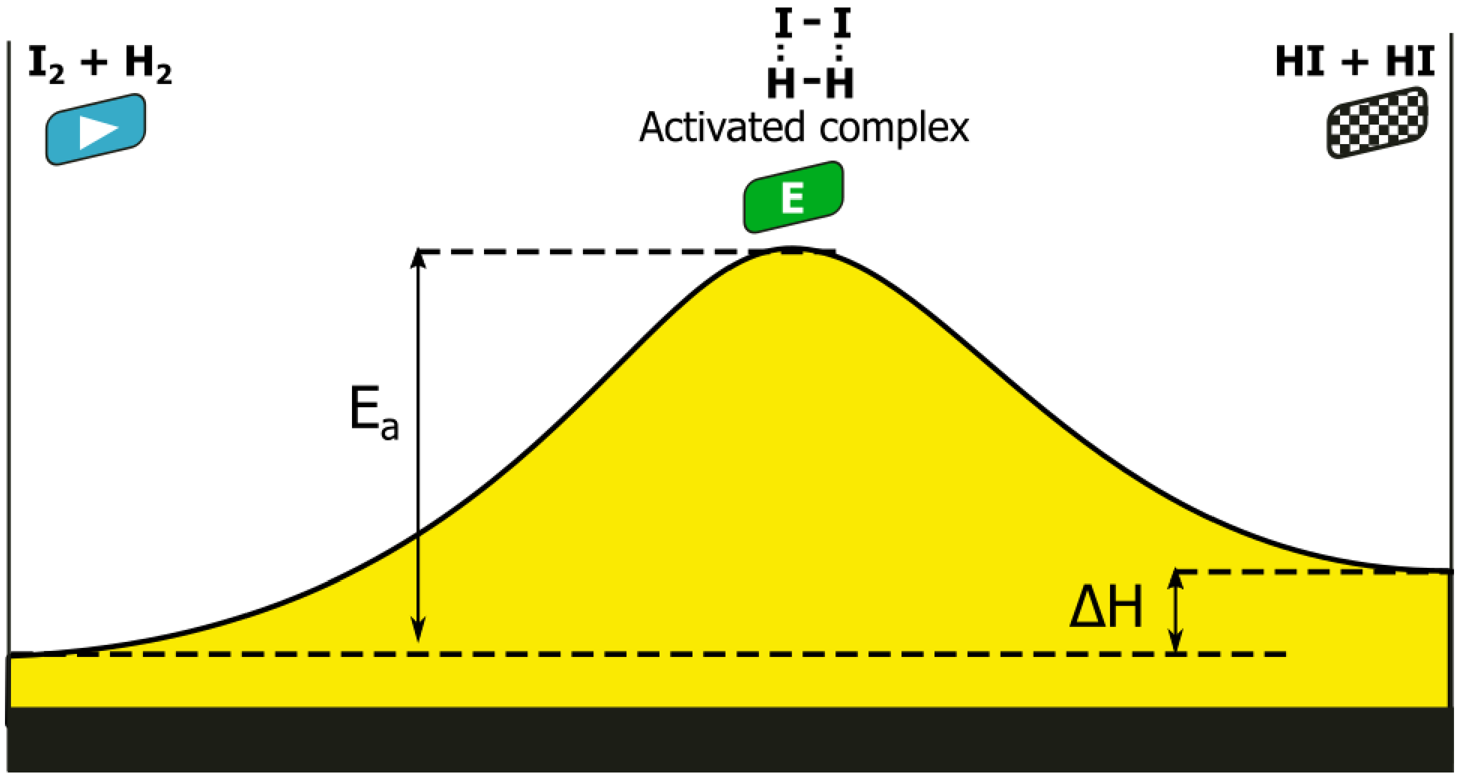
Understanding the activation energy



Reaction Coordinate Diagram for HI Formation

Understanding the activation energy



Reaction Coordinate Diagram for HI Formation

Mind the temperature

$$k = Ae^{-\frac{E_a}{RT}}$$

T	E_a		
	40 kJ/mol	80 kJ/mol	120 kJ/mol
298 K	$5 \cdot 10^{-8}$	$2 \cdot 10^{-15}$	$9 \cdot 10^{-23}$
400 K	$3 \cdot 10^{-6}$	$1 \cdot 10^{-11}$	$4 \cdot 10^{-17}$
600 K	$2 \cdot 10^{-4}$	$5 \cdot 10^{-8}$	$1 \cdot 10^{-11}$
800 K	$2 \cdot 10^{-3}$	$3 \cdot 10^{-6}$	$7 \cdot 10^{-9}$

Fats going rancid

Phone losing battery faster

Iron corrosion

Boooom!!

Explosives release a large amount of energy when they burn. A small increase in temperature (such as that produced by a match or a spark) is enough to initiate the reaction locally. The heat released further raises the temperature of the surrounding material. This, in turn, accelerates the reaction even more, creating a positive feedback loop that rapidly leads to an explosion.

Challenge question

For the reaction of formation of hydrogen iodide from its elements at 400 °C, the activation energy is 172 kJ mol^{-1}. Calculate the increase in the reaction rate when the temperature is raised from 400 °C to 500 °C.