ChemE 2200 – Chemical Kinetics Lecture 4

Today:

Reversible Reactions, cont'd

“Can reaction rates (kinetics) predict equilibrium concentrations (thermodynamics)?”

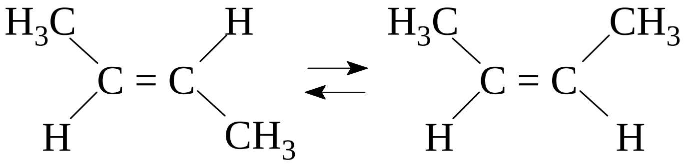
“Can equilibrium concentrations (thermodynamics) predict reaction rates (kinetics)?”

Temperature Dependence of Reaction Rates

“Why do reaction rates generally increase *exponentially* with temperature?”

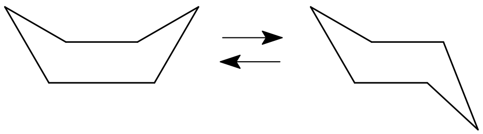
Recap: Reversible Isomerization in a Batch Reactor

$CH_3N{=}C \rightleftarrows CH_3C{\equiv}N$



trans

cis



boat

chair

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \qquad \text{if both reactions are elementary} \;\Rightarrow\; \frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

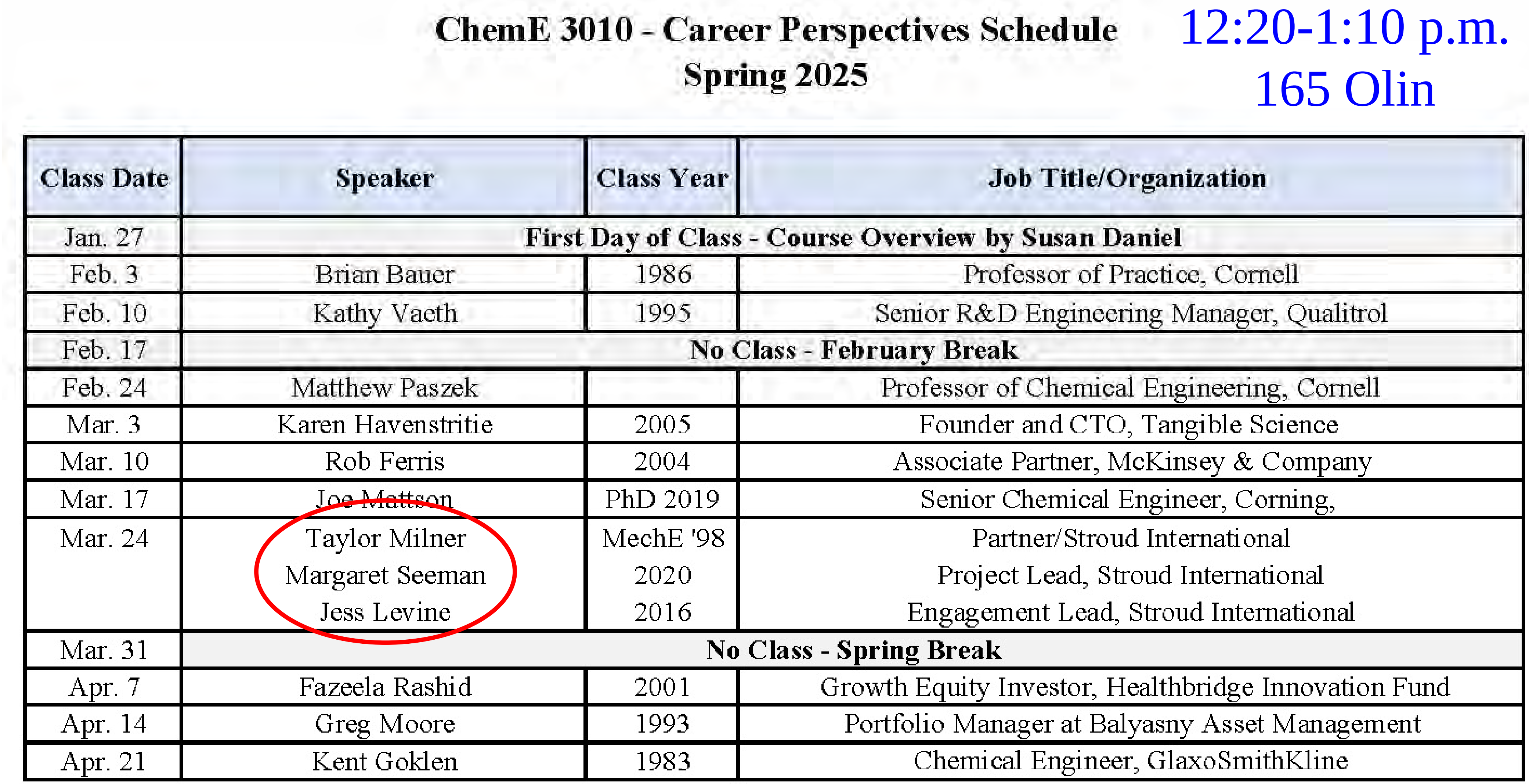
$$\text{mass balance} \Rightarrow \text{mol balance} \Rightarrow [B] = [A]_0 - [A] \;\Rightarrow\; \frac{d[A]}{dt} = -(k_1 + k_{-1})[A] + k_{-1}[A]_0$$

$$[A] = \left[\frac{k_1 e^{-(k_1 + k_{-1})t} + k_{-1}}{k_1 + k_{-1}}\right][A]_0$$

Reading for Kinetics Lecture 5: McQuarrie & Simon, Chp 29.1-29.2.

Career Guidance

Mondays
12:20-1:10 p.m.
165 Olin



ChemE 3010 - Career Perspectives Schedule
Spring 2025

Class Date	Speaker	Class Year	Job Title/Organization
Jan. 27	**First Day of Class - Course Overview by Susan Daniel**		
Feb. 3	Brian Bauer	1986	Professor of Practice, Cornell
Feb. 10	Kathy Vaeth	1995	Senior R&D Engineering Manager, Qualitrol
Feb. 17	**No Class - February Break**		
Feb. 24	Matthew Paszek		Professor of Chemical Engineering, Cornell
Mar. 3	Karen Havenstritie	2005	Founder and CTO, Tangible Science
Mar. 10	Rob Ferris	2004	Associate Partner, McKinsey & Company
Mar. 17	Joe Mattson	PhD 2019	Senior Chemical Engineer, Corning,
Mar. 24	Taylor Milner Margaret Seeman Jess Levine	MechE '98 2020 2016	Partner/Stroud International Project Lead, Stroud International Engagement Lead, Stroud International
Mar. 31	**No Class - Spring Break**		
Apr. 7	Fazeela Rashid	2001	Growth Equity Investor, Healthbridge Innovation Fund
Apr. 14	Greg Moore	1993	Portfolio Manager at Balyasny Asset Management
Apr. 21	Kent Goklen	1983	Chemical Engineer, GlaxoSmithKline

Margaret Seeman '20

Hometown: Darien, CT

JOURNEY TO CORNELL: During high school, I fell in love with the study of chemistry and knew that I wanted to become a chemical engineer. My father is an Engineering alum of Cornell University and when we visited, I knew I could see myself loving it here. I also realized that becoming a Cornell engineer required a tenacious amount of work and a heavy winter coat!

LEADERSHIP POSITIONS AND ACCOMPLISHMENTS: After affiliating with Chemical Engineering, I joined AIChE (American Institute of Chemical Engineers). My senior year, I was the AIChE social chair and had a blast planning the annual BBQ and arranging times for ChemEs to get together outside of the classroom. During the department holiday party, our AIChE executive board performed a skit, which told a story about each of our amazing professors. Being a part of AIChE was an important part of my career at Cornell. It created a family of people all studying the same major, and at the same time supporting each other. Spring semester of my senior year, I was a teaching assistant for Analysis of Separations Processes, a junior ChemE class. I was not only able to connect with the junior class, but I was also able to help students understand and work through challenging material that I had learned the year before. All four years I also participated in my sorority: Delta Gamma. In 2019, I was the Vice President of Social Standards for the Cornell chapter.

ADVICE FOR FUTURE STUDENTS: Embrace every second in the Smith School of Chemical and Biomolecular Engineering and every connection with students and professors. Cornell Chemical Engineering is something so special. The size of the major allows for students to become a family, as the Class of 2020 has. The faculty and staff are amazing. Whether it was class related or career related, I knew if I asked for help, I would find it in Olin Hall. I am so happy to go out into my post graduate life with these amazing connections and lifelong friends.

Olin Hall News
2020

Mathematical Model for a First-Order Reversible Reaction, cont'd

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B}$$

If we seek only the concentrations at equilibrium ($t \to \infty$),
we may apply kinetics in a more direct manner.

At any time,

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{B}]$$

At equilibrium,

$$\frac{d[\mathrm{A}]}{dt} = 0 = -k_1[\mathrm{A}]_{\mathrm{eq}} + k_{-1}[\mathrm{B}]_{\mathrm{eq}}$$

steady state

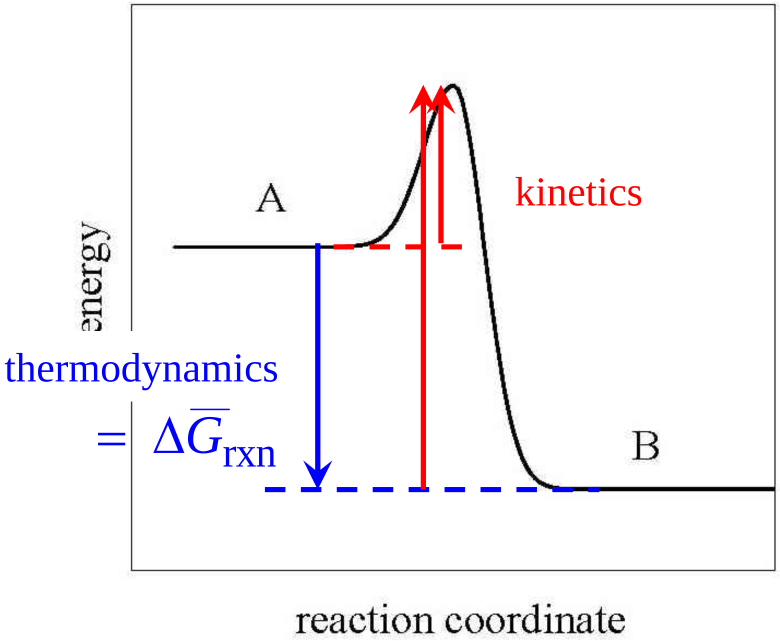
$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_1}{k_{-1}} = K_{\mathrm{eq}} = e^{-\Delta\overline{G}_{\mathrm{rxn}}/RT}$$

Mathematical Model for a First-Order Reversible Reaction, cont'd

$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_1}{k_{-1}} = K_{\mathrm{eq}} = e^{-\Delta \overline{G}_{\mathrm{rxn}} / RT}$$

If we know reaction rates (chemical kinetics),
we can calculate equilibrium concentrations (chemical thermodynamics).

How to reconcile with the reaction-coordinate energy-level diagram?



If we know equilibrium concentrations (chemical thermodynamics)
can we calculate reaction rates (chemical kinetics)? No.

Exception: if one knows ΔG_{rxn} to the unstable intermediate (Transition State Theory).

Temperature Dependence of Reaction Rates

A → products $\quad r_{rxn} = k[A]^n$

Independent of *T*

Increases exponentially with *T*. Why?

Because $\Delta K.E. \approx 0$, excited states are a continuum.

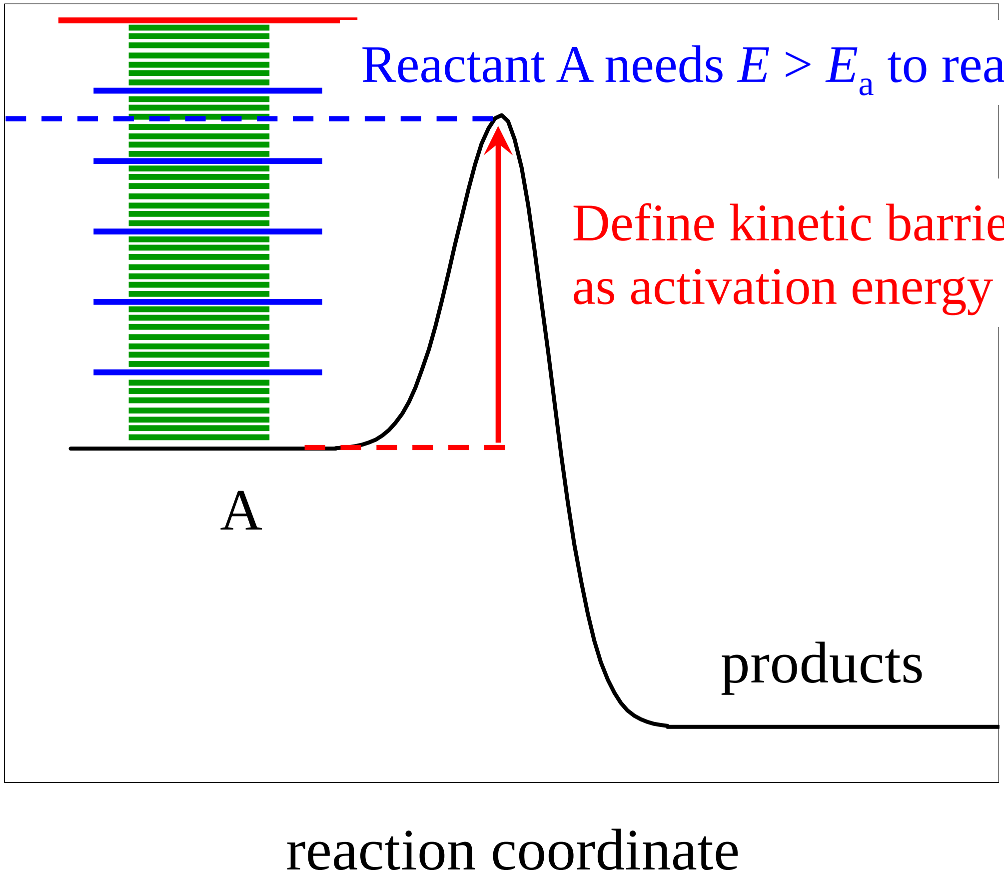
ground state = 0

translational: $v_x = v_y = v_z = 0$

rotational: J’s = 0

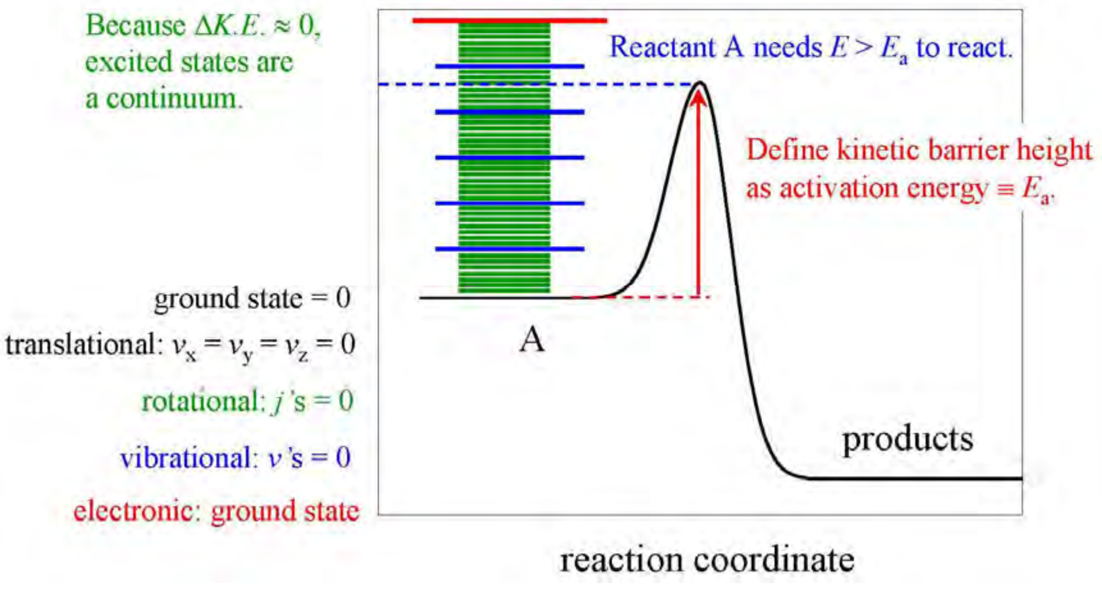
vibrational: *v*’s = 0

electronic: ground state

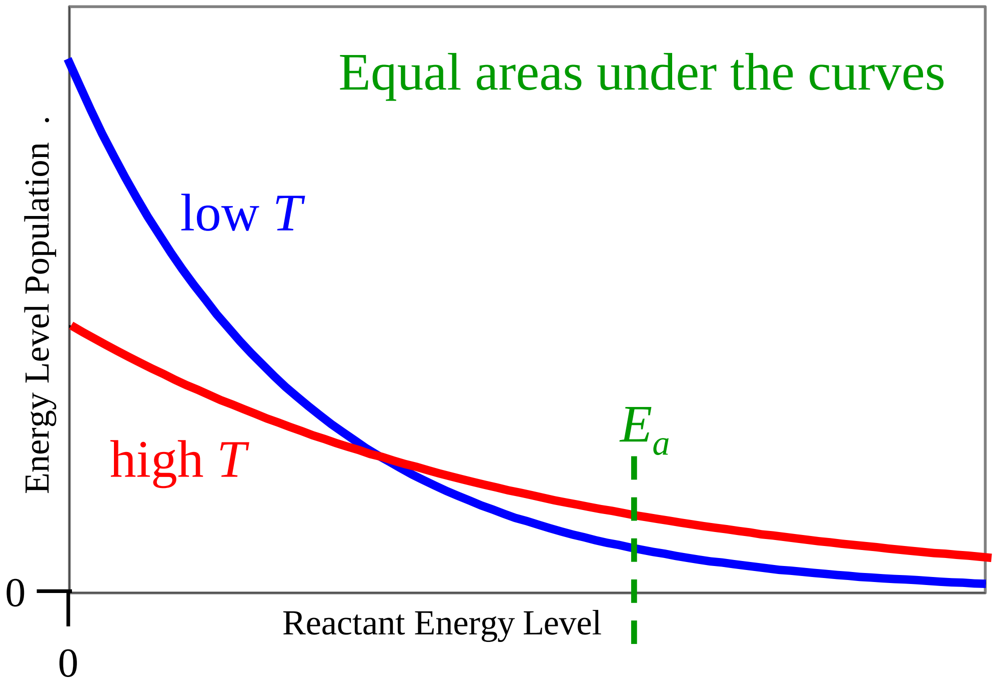


Reactant A needs $E > E_a$ to react.

Define kinetic barrier height as activation energy $\equiv E_a$.



Boltzmann distribution:
population $\propto e^{-E/RT}$



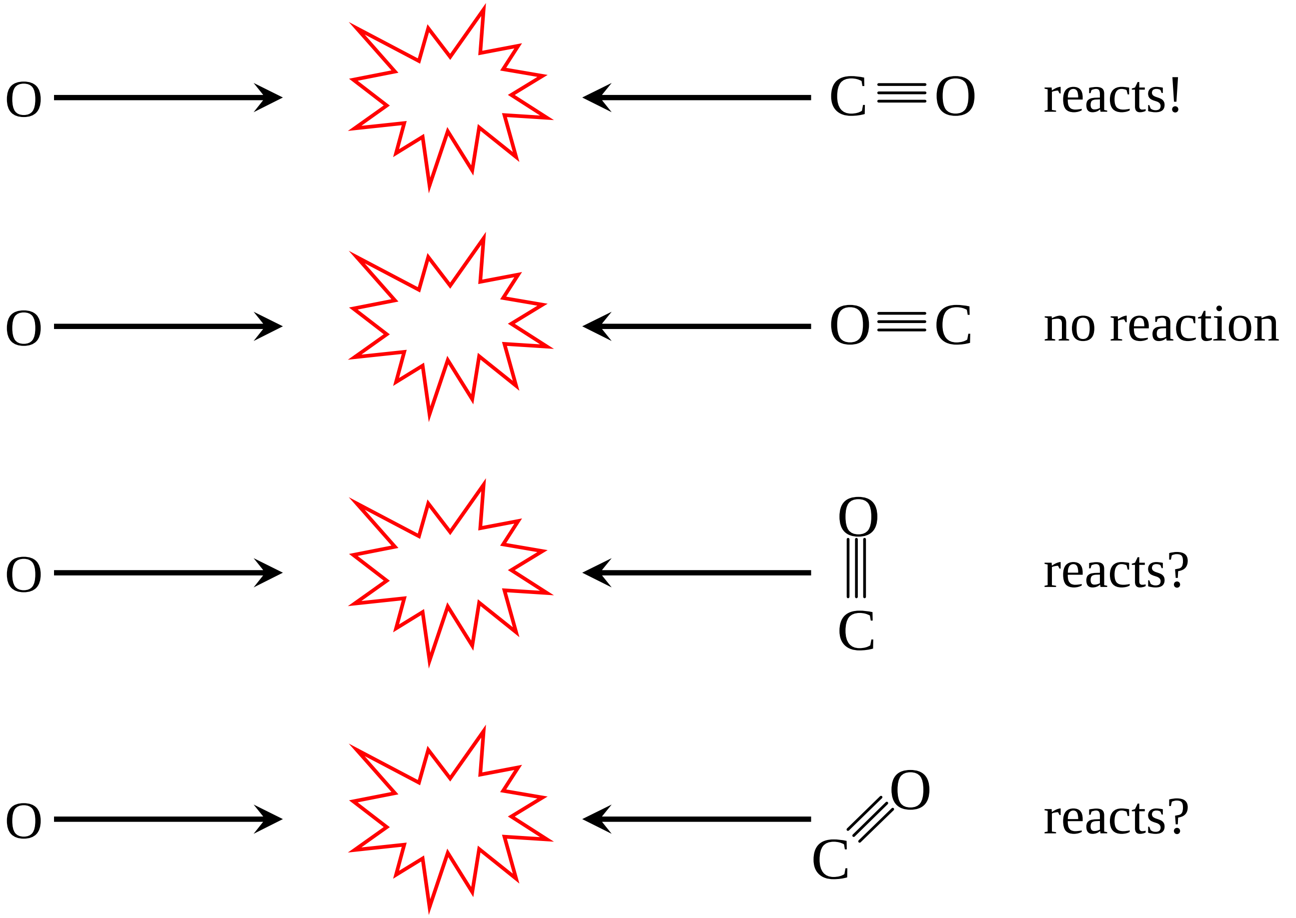
$$\text{reactants with } E > E_a \propto \frac{1}{RT}\int_{E_a}^{\infty} e^{-E/RT} \propto \frac{RT}{RT}\left(e^{-E_a/RT} - 0\right) \propto e^{-E_a/RT}$$

Criteria for Chemical Reaction

Consider the bi-molecular reaction O + C≡O $\rightarrow$ O=C=O (linear molecule)

The collision of O and C≡O must have sufficient energy: $E_{\text{collision}} > E_a$

The collision of O and C≡O must have the proper orientation and the proper trajectory.



Criteria for Chemical Reaction

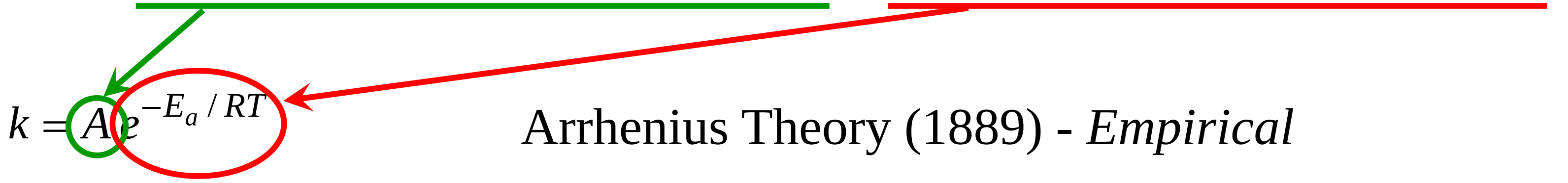
Consider the bi-molecular reaction $O + C{\equiv}O \rightarrow O{=}C{=}O$ (linear molecule)

The collision of O and C≡O must have sufficient energy: $E_{\text{collision}} > E_a$

The collision of O and C≡O must have the proper orientation.

$$r_{\text{rxn}} = k\,[\text{O}][\text{CO}]$$

Qualitatively, k = (rate of attempts) × (probability that attempt is successful)



$$k = (\underline{\text{rate of attempts}) \times [(\text{steric factor}}) \times \underline{(\text{Boltzmann energy distribution})}]$$

$$k = \boxed{A}\,\boxed{e^{-E_a/RT}}$$

Arrhenius Theory (1889) - *Empirical*

A is the Arrhenius 'pre-exponential', aka 'frequency factor.'

Arrhenius Theory assumes A is independent of temperature: $A \propto T^0$

Kinetic Theory of Gases: $A \propto T^{1/2}$

Transition State Theory: $A \propto T^1$ for gas-phase reactions

The temperature dependence of the Boltzmann factor
usually overwhelms any temperature dependence of A.

Arrhenius Parameters A and E_a from Experimental Data

Example: A + B → products $r_{rxn} = k\,[A]^n[B]^m$

Measure r_{rxn} at different temperatures and concentrations. Calculate k at each temperature.

Assume Arrhenius Theory:

$$k = A\,e^{-E_a/RT}$$

$$\underbrace{\ln k}_{y} = \ln A + \underbrace{\frac{-E_a}{R}}_{\text{slope}}\,\underbrace{\frac{1}{T}}_{x}$$

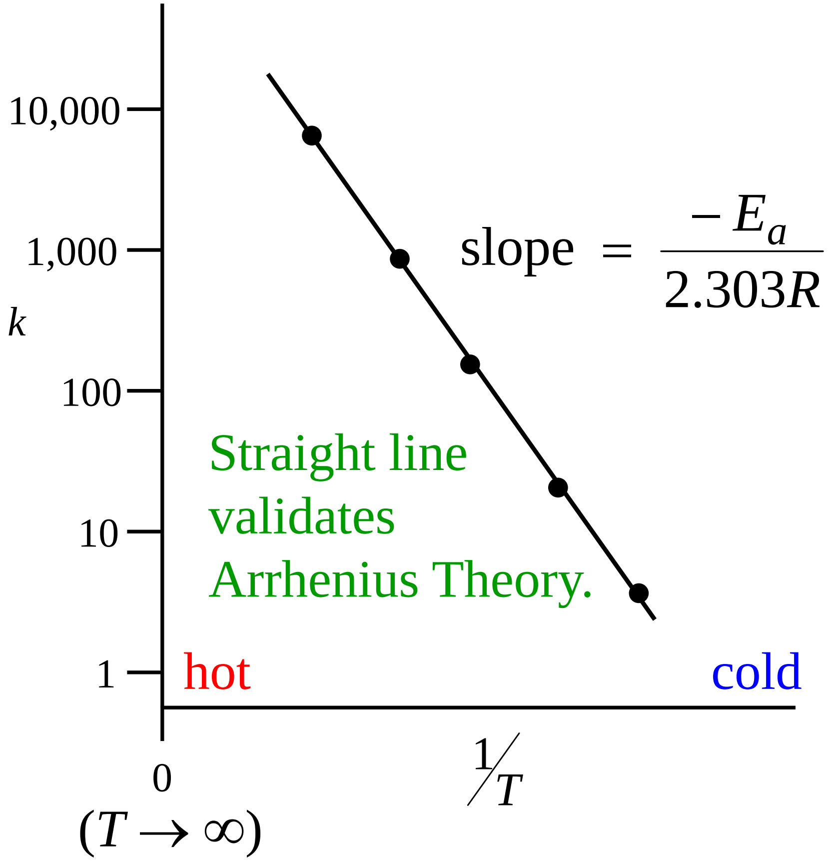
or use semi-log paper.

$$2.303\log k = 2.303\log A + \frac{-E_a}{R}\,\frac{1}{T}$$

$$\underbrace{\log k}_{y} = \log A + \underbrace{\frac{-E_a}{2.303R}}_{\text{slope}}\,\underbrace{\frac{1}{T}}_{x}$$

Goal: A straight line to verify the assumption.

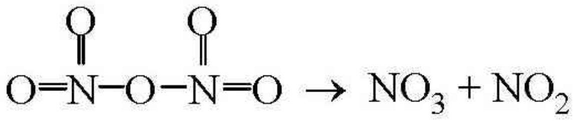
Plot ln k vs. 1/T



$$\text{slope} = \frac{-E_a}{2.303R}$$

Straight line validates Arrhenius Theory.

Arrhenius Theory - Typical Parameters

Chemical Reaction	Activation Energy, E_a		$e^{-E_a/kT}$		A	elementary?
	kJ/mol	eV/molecule	300 K	600 K		
 $\mathrm{O{=}\overset{\overset{O}{\|}}{N}{-}O{-}\overset{\overset{O}{\|}}{N}{=}O \rightarrow NO_3 + NO_2}$	5	0.05	$0.1 \xrightarrow{\times 4}$	0.4	10^{15}/sec	
$CH_3{-}CO\bullet \rightarrow \bullet CH_3 + CO$	43	0.45	3×10^{-8}	2×10^{-4}	10^{15}/sec	
$CH_3{-}CH_3 \rightarrow \bullet CH_3 + \bullet CH_3$	380	4.0	$10^{-66} \xrightarrow{\times 10^{33}}$	10^{-33}	10^{17}/sec	
$\bullet CH_3 + \bullet CH_3 \rightarrow CH_3{-}CH_3$	~0	~0	1	1	10^{11} L/(mol·sec)	
$NO + O_3 \rightarrow NO_2 + O_2$	11	0.12	0.01	0.1	10^{12}	
$NO + Cl_2 \rightarrow NOCl + \bullet Cl$	85	0.89	2×10^{-15}	4×10^{-8}	10^{12}	
$2NO_2 \rightarrow 2NO + O_2$	114	1.2	2×10^{-20}	10^{-10}	10^{11}	
$2O_3 \rightarrow 3O_2$	144	1.5	10^{-25}	3×10^{-13}	10^{12}	

$0 \leq E_a < 400$ kJ/mol

For $XY \rightarrow X + Y$
$A \approx$ vibrational frequency
$A \approx 10^{15}$ - 10^{17}/sec

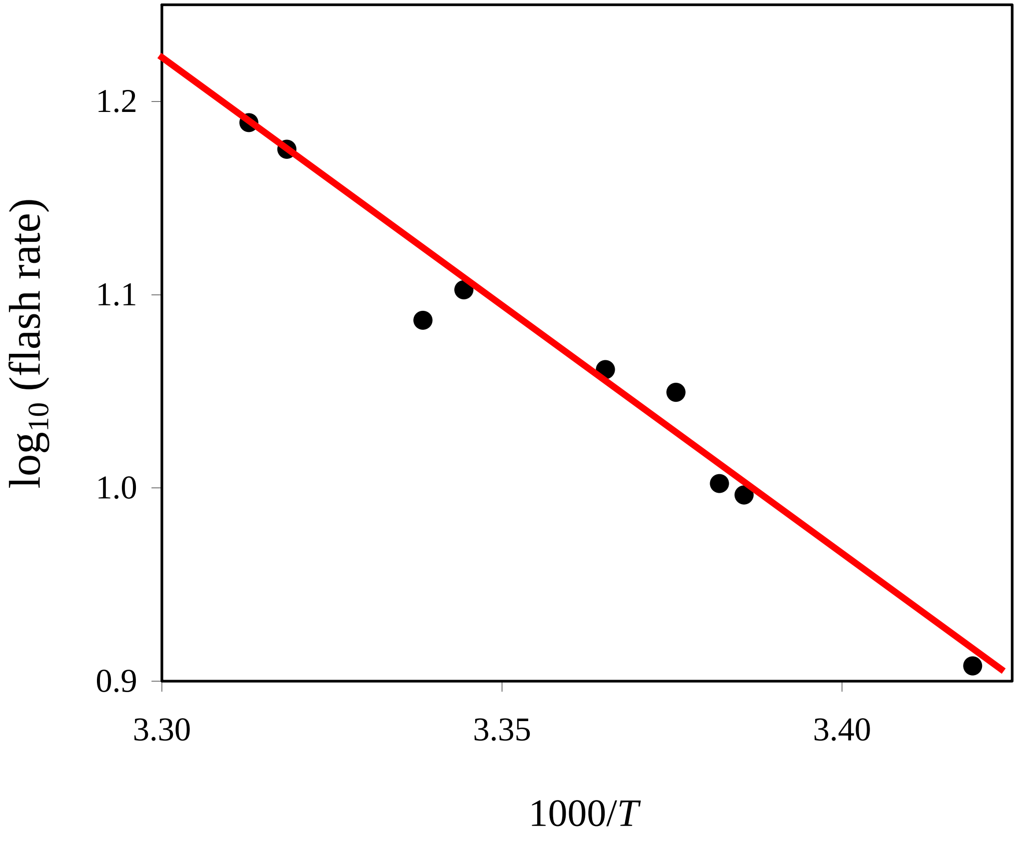
For $X + Y \rightarrow XY$
$A \approx$ collision rate
$A \approx 10^{10}$ - 10^{12} L/(mol·sec)

Unconventional Applications of the Arrhenius Law

Flashing Rate in Fireflies

Activation Energy for Firefly Flashing = 51 kJ/mol

T(ºC)	*T*(ºF)	flashes/min
28.7	83.7	15.5
28.2	82.8	15.0
25.9	78.5	12.7
26.4	79.5	12.2
24.0	75.2	11.5
23.1	73.6	11.2
22.5	72.6	10.1
22.2	72.0	9.9
19.3	66.8	8.1



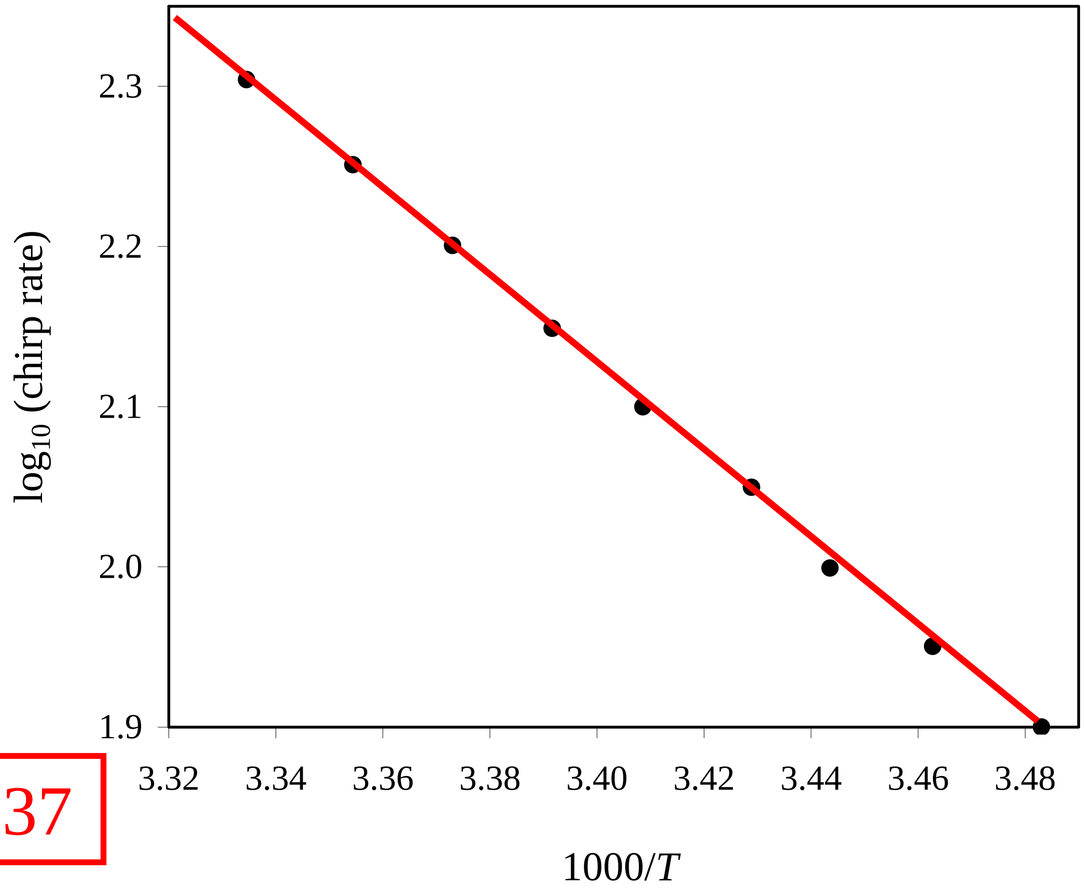
C. D. Synder and A. v't H. Snyder, *Amer. J. Physiol.* **51**, 536 (1920).
W. J. Crozier, *J. Gen. Physiol.* **7**, 136 (1936).
Keith J. Laider, University of Ottawa, *J. Chemical Education*, **49** 344 (1972).

Unconventional Applications of the Arrhenius Law

Chirping Rate in Crickets

Activation Energy for Cricket Chirping = 56 kJ/mol

T(°C)	*T*(°F)	chirps/min
26.7	80.1	201
25.0	76.9	178
23.3	74.0	159
21.7	71.0	141
20.2	68.4	126
18.5	65.3	112
17.2	63.0	100
15.6	60.2	89
14.0	57.1	79

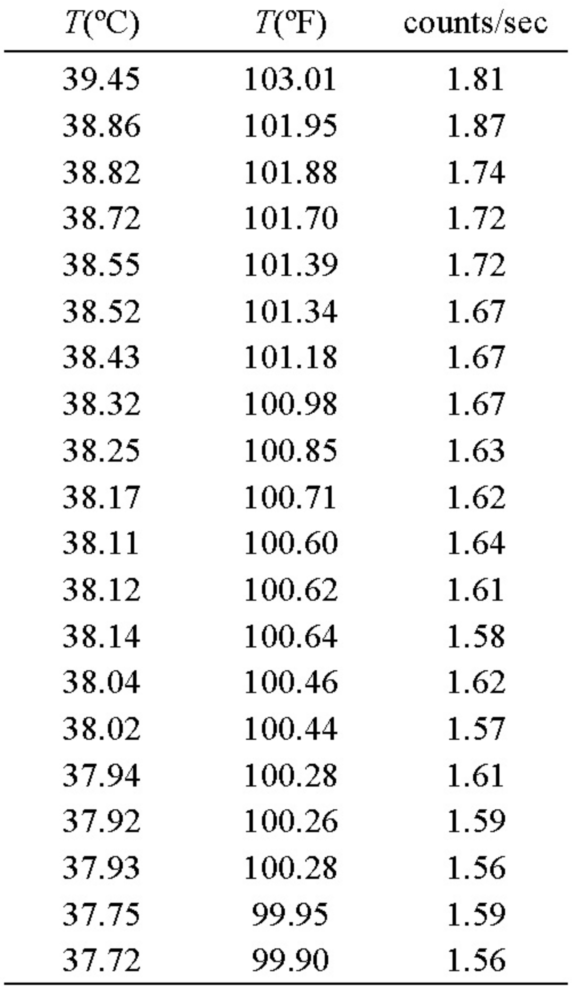


T(°F) = chirps in 15 seconds + 37

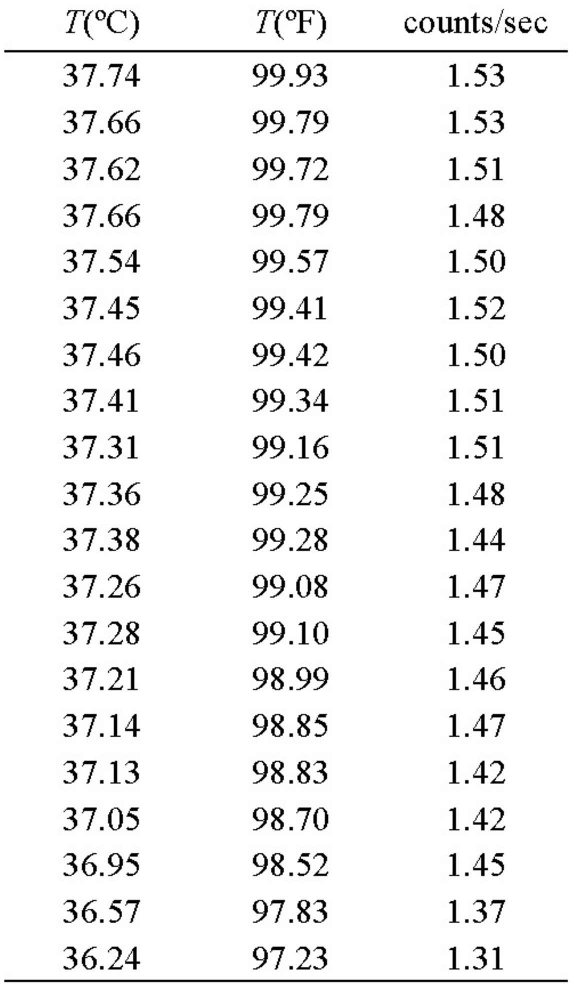
C. A. Bessey and E. A. Bessey, *Amer. Natur.* **32**, 263 (1898).
R. T. Edes, *Amer. Natur.* **33**, 935 (1899).
A. F. Shulls, *Can. Entomol.* **39**, 213 (1907).

Unconventional Applications of the Arrhenius Law

Counting Rate in Humans



T(ºC)	*T*(ºF)	counts/sec
39.45	103.01	1.81
38.86	101.95	1.87
38.82	101.88	1.74
38.72	101.70	1.72
38.55	101.39	1.72
38.52	101.34	1.67
38.43	101.18	1.67
38.32	100.98	1.67
38.25	100.85	1.63
38.17	100.71	1.62
38.11	100.60	1.64
38.12	100.62	1.61
38.14	100.64	1.58
38.04	100.46	1.62
38.02	100.44	1.57
37.94	100.28	1.61
37.92	100.26	1.59
37.93	100.28	1.56
37.75	99.95	1.59
37.72	99.90	1.56



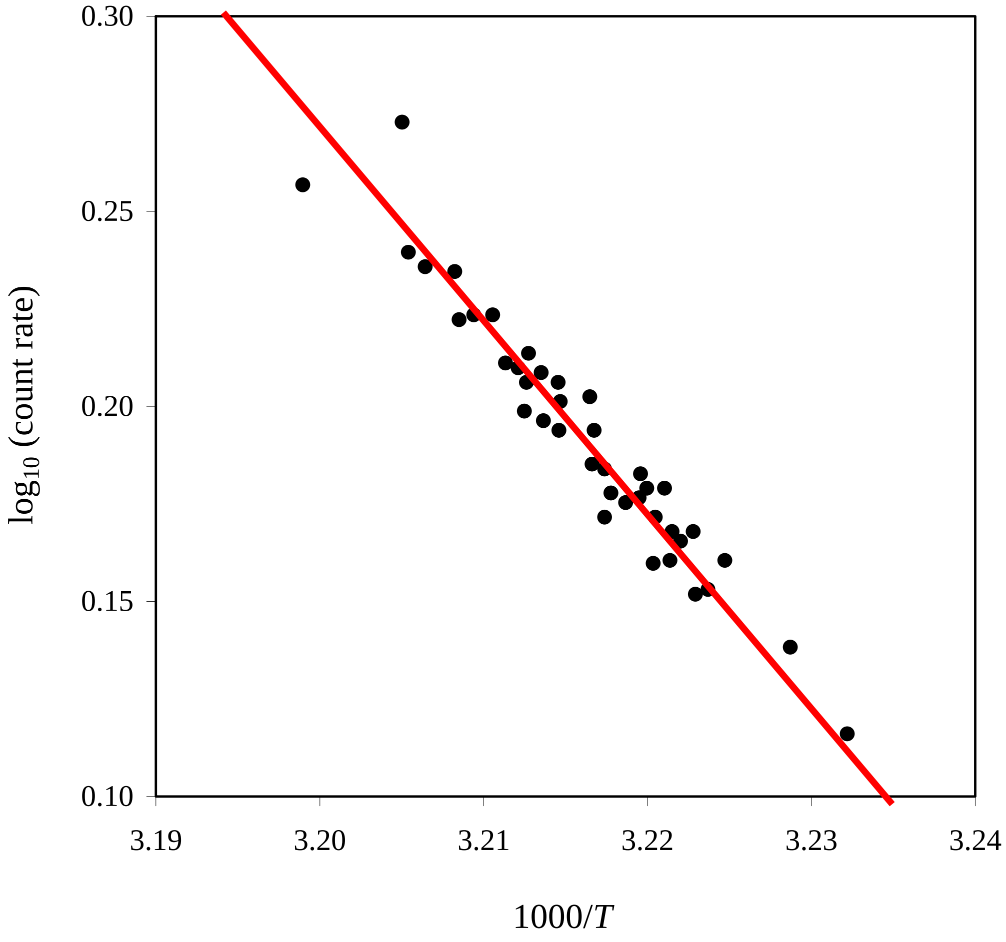
T(ºC)	*T*(ºF)	counts/sec
37.74	99.93	1.53
37.66	99.79	1.53
37.62	99.72	1.51
37.66	99.79	1.48
37.54	99.57	1.50
37.45	99.41	1.52
37.46	99.42	1.50
37.41	99.34	1.51
37.31	99.16	1.51
37.36	99.25	1.48
37.38	99.28	1.44
37.26	99.08	1.47
37.28	99.10	1.45
37.21	98.99	1.46
37.14	98.85	1.47
37.13	98.83	1.42
37.05	98.70	1.42
36.95	98.52	1.45
36.57	97.83	1.37
36.24	97.23	1.31

H. Hoagland, Sci. Mon. **56** 56 (1943).

Unconventional Applications of the Arrhenius Law

Counting Rate in Humans

Activation Energy for Counting = 95 kJ/mol



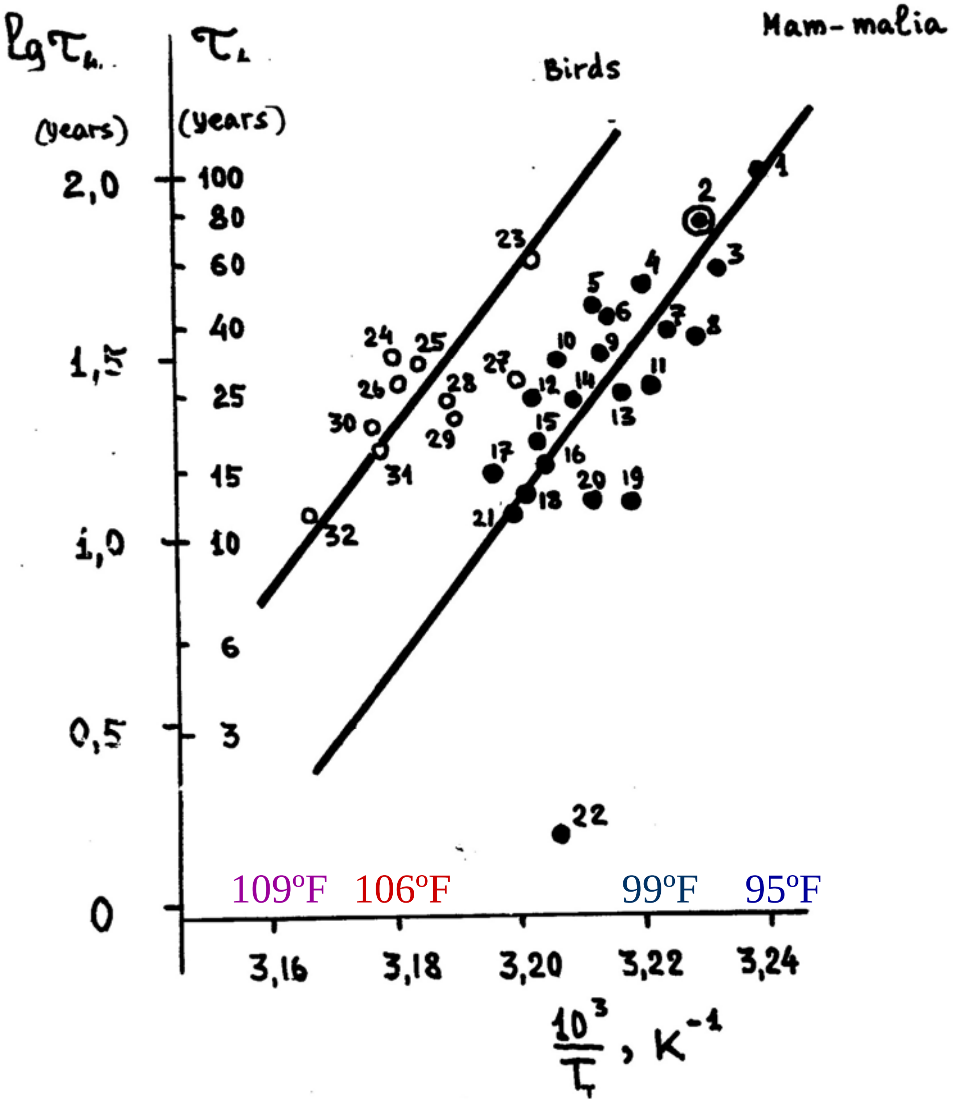
H. Hoagland, Sci. Mon. **56** 56 (1943).

Unconventional Applications of the Arrhenius Law

Longevity as a Function of Body Temperature

1- Whale
2- Man
3- Elefant
4-Rhinoceros
5- Donkey
6- Horse
7- } Monkey
8- }
9- Bear br.
10- Bear white
11· Camel
12· Elk
13· Leopard
14· Cow
15· Pig
16· Cat
17· Wolf
18· Rabbit
19· Jackal
20 Dog
21 Goat
22 Mouse

23 Ostrich
24 Goose
25 Pigeon
26 Sea-gull
27 Penguin
28 Flamingo
29
30 Hen
31 Duck
32 Turkey



Activation Energy = 380 to 420 kJ/mol

Svante August Arrhenius (1859-1927)

1884 – PhD in Physical Chemistry at the University of Uppsala: “Investigations on the Galvanic Conductivity of Electrolytes.”

In forming a solution, a salt disassociates into charged particles, called ‘ions.’

Arrhenius proposed that chemical reactions in solution were reactions between ions.

Earned a 4th-Class Degree.

Upon defense, reclassified as a 3rd-Class Degree.

1903 – His PhD work is awarded a Nobel Prize in Chemistry.

1889 – Proposed the concept of activation energy to explain why most reactions require heat to proceed.

1896 – In his theory to explain the ice ages, was the first to use basic principles of physical chemistry to calculate temperature increases caused by atmospheric CO_2.

First proposal of the greenhouse effect.