CBPF
Centro Brasileiro de Pesquisas Físicas

Scaling and Renormalization in the Kinetics of Rate Processes

Valter H. Carvalho-Silva
Goias State University
Laboratory for Modeling of Physical and Chemical Transformations

UEG

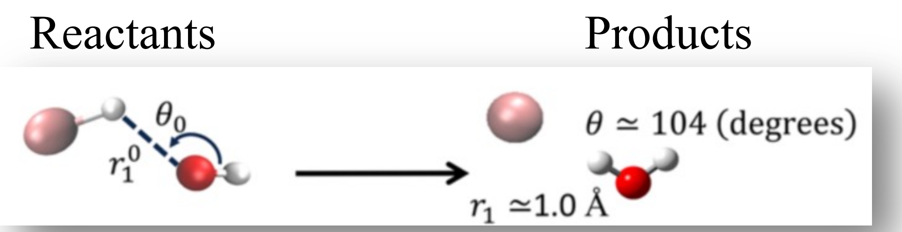
MPhysChem Laboratory

@lab_mphyschem
www.mphyschem.com

Content

1.
2.
3. A

Scaled Rate Processes



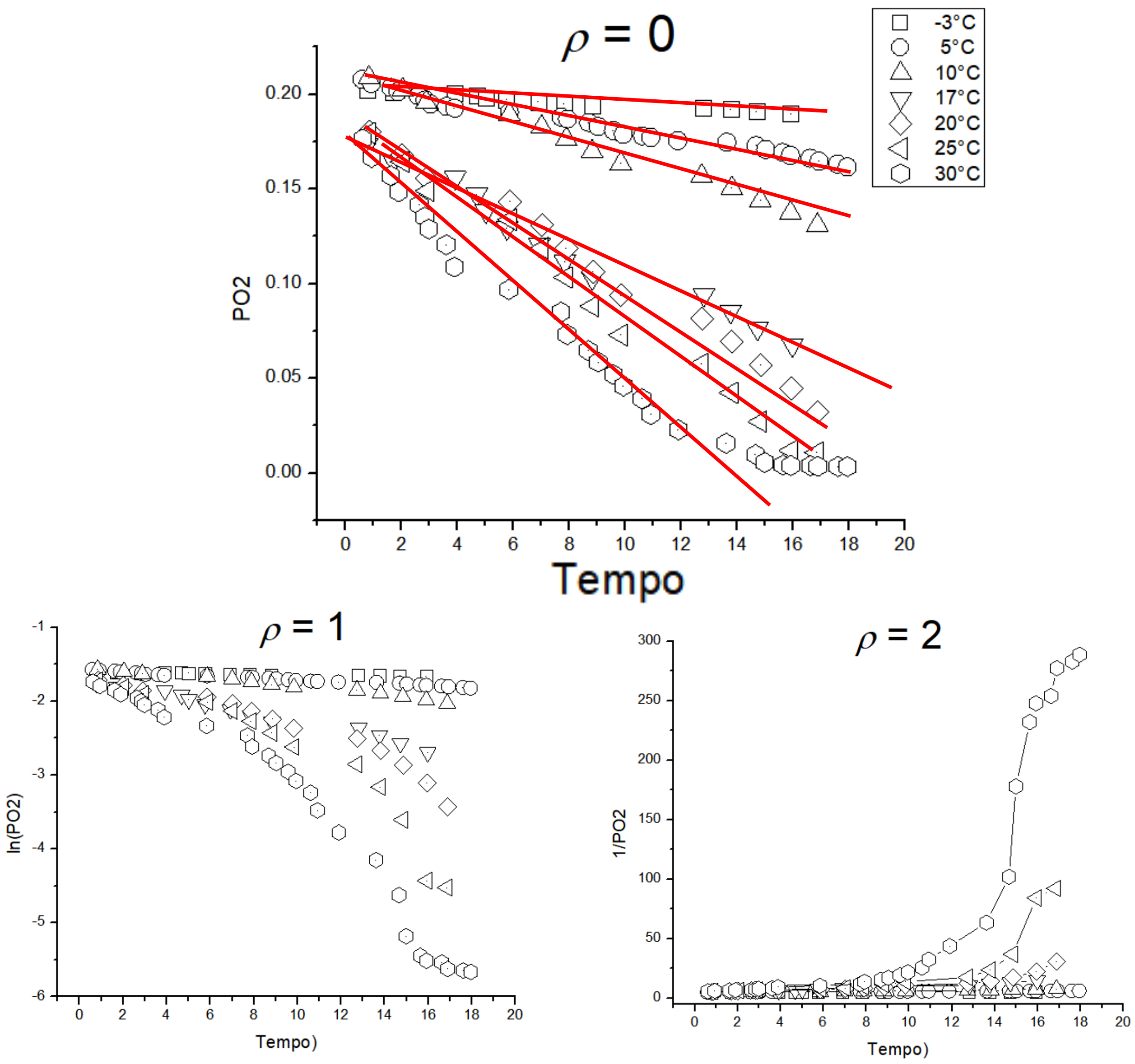
- **van`t Hoff law.**

$$aA + bB \cdots \rightarrow cC \cdots$$

$$-\frac{1}{a}\frac{d}{dt}[A] = -\frac{1}{b}\frac{d}{dt}[B] = \frac{1}{c}\frac{d}{dt}[C] = \cdots$$

$$-\frac{\partial}{\partial t}[A] = k(T)[A]^{\rho}$$

Respiration Rate of leaves



M. Nishiyama, S. Kleijn, V. Aquilanti, and T. Kasai, Chem Phys Lett **482**, 325 (2009).

Scaled Rate Processes

- Arrhenius – van`t Hoff law.

$$\mathrm{A} + \mathrm{B} \xrightarrow{k(T)} \text{[illegible]}$$

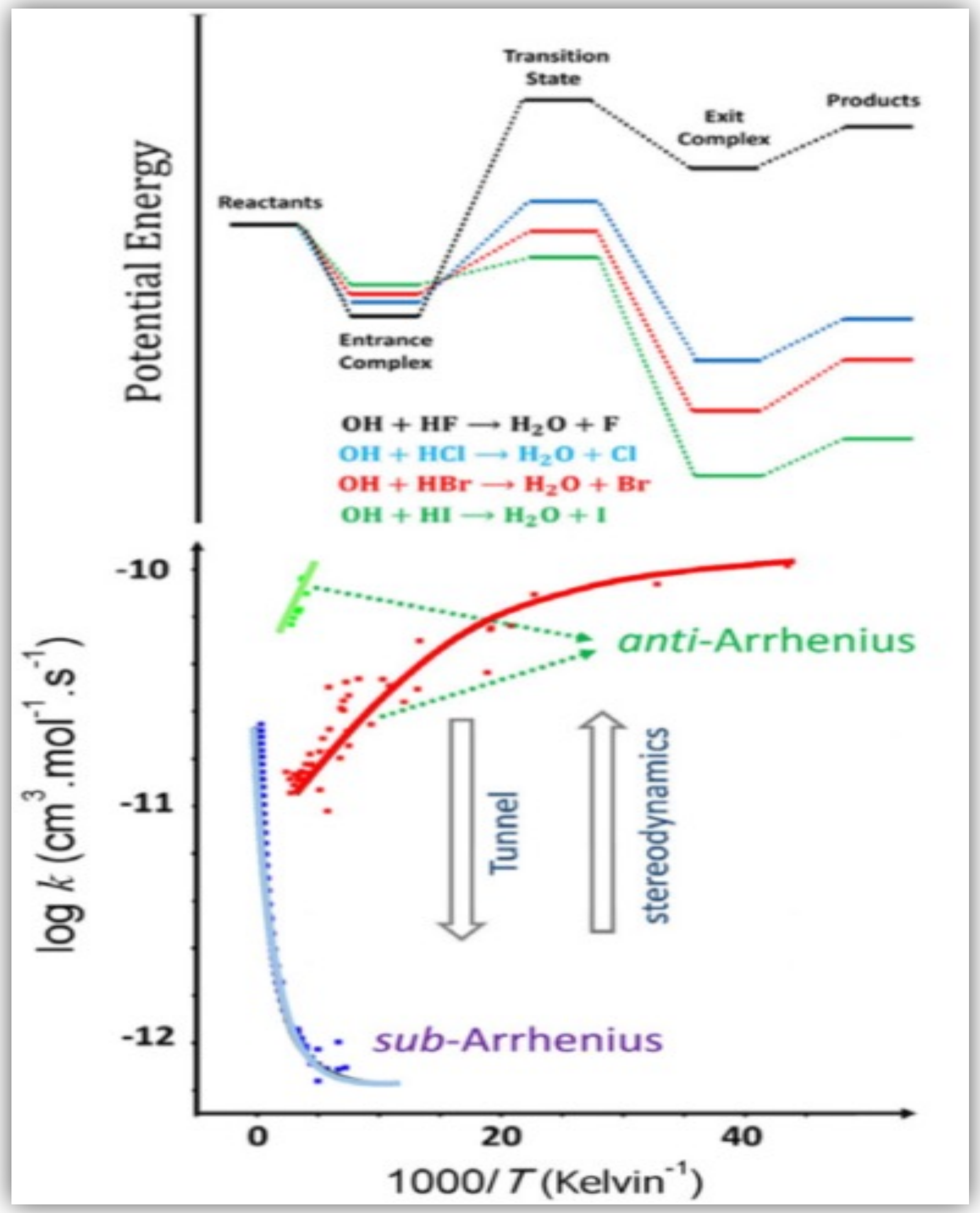
Activation Energy Interpretation.

Scaled Arrhenius Plot

$$\ln k(T) = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)$$

$$E_a(\beta) = -\frac{\mathrm{d}}{\mathrm{d}\,\beta}\ln k(\beta)$$

$\beta = 1/k_B T$



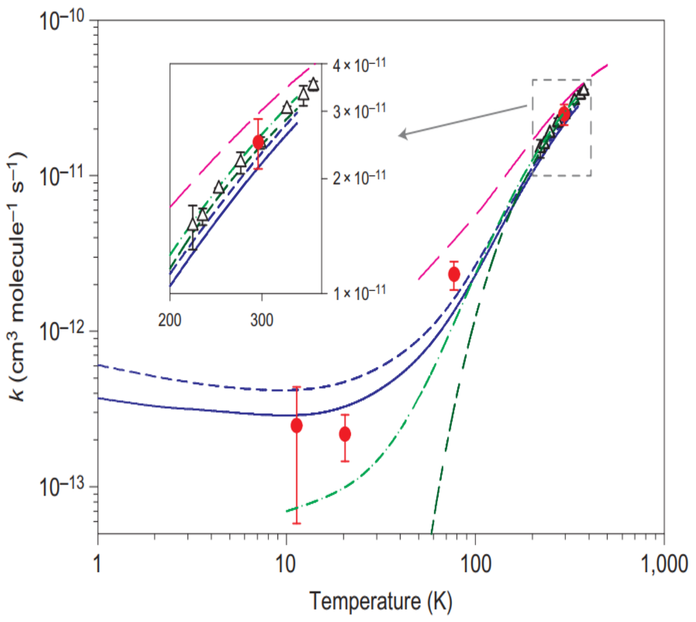
N. D. Coutinho, *et al*, J Comput Chem **39**, 2508 (2018)

non-Arrhenius cases

nature chemistry ARTICLES
PUBLISHED ONLINE: 12 JANUARY 2014 | DOI: 10.1038/NCHEM.1835

The rate of the $F + H_2$ reaction at very low temperatures

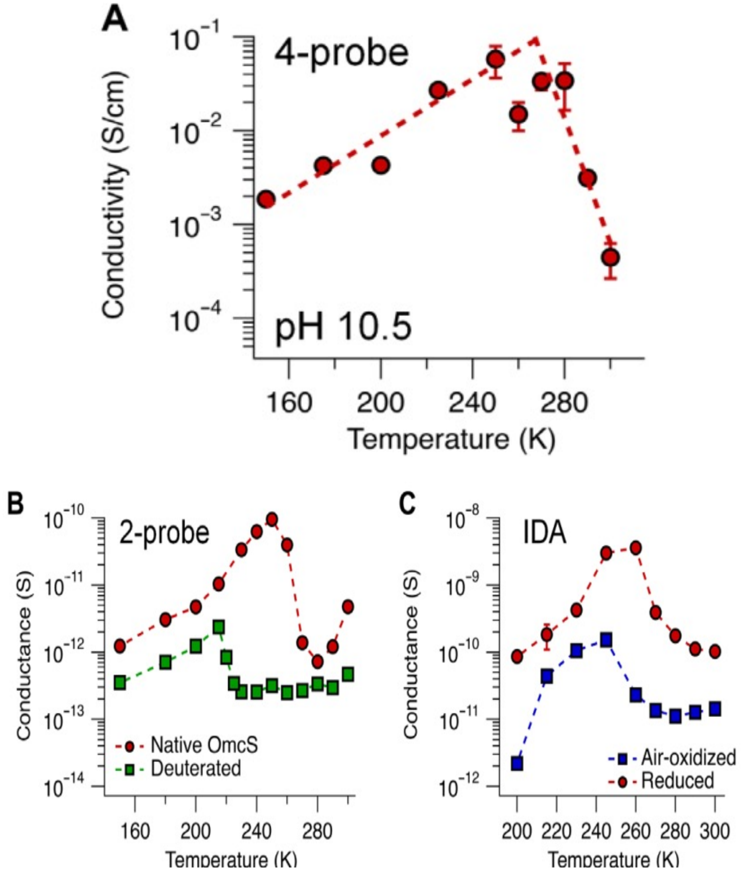
Meryem Tizniti[1], Sébastien D. Le Picard[1], François Lique[2], Coralie Berteloite[1], André Canosa[1], Millard H. Alexander[3]* and Ian R. Sims[1]*



Science Advances
Current Issue First release papers Archive About
HOME > SCIENCE ADVANCES > VOL. 8, NO. 19 > A 300-FOLD CONDUCTIVITY INCREASE IN MICROBIAL CYTOCHROME NANOWIRES DUE TO TEMPERATURE-...
RESEARCH ARTICLE | BIOPHYSICS

A 300-fold conductivity increase in microbial cytochrome nanowires due to temperature-induced restructuring of hydrogen bonding networks

PETER J. DAHL, SOPHIA M. YI, YANGQI GU, ATANU ACHARYA, CATHARINE SHIPPS, JENS NEU, J. PATRICK O'BRIEN, URIEL N. MORZAN, SUBHAJYOTI CHAUDHURI, MATTHEW J. GUBERMAN-PFEFFER, DENNIS VU, SIBEL EBRU YALCIN, VICTOR S. BATISTA, AND NIKHIL S. MALVANKAR

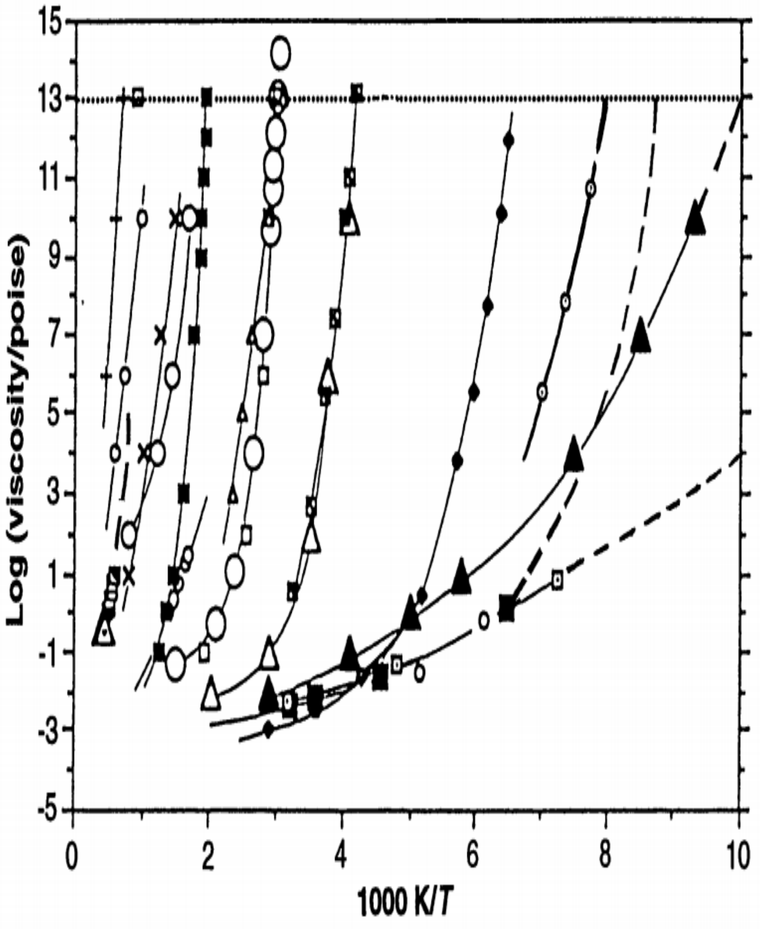


ARTICLES

Formation of Glasses from Liquids and Biopolymers

C. A. Angell[1]
+ See all authors and affiliations

Science 31 Mar 1995:
Vol. 267, Issue 5206, pp. 1924-1935
DOI: 10.1126/science.267.5206.1924



Scaled Rate Processes

➢ **Empirical adaptation from Tsallis statistics.**

Tsallis Statistics

$$S_q = \frac{k}{q-1}\sum_{i=1}^{W} p_i(1-p_i^{q-1}) \qquad p_i = \frac{[1-\beta(q-1)\varepsilon_i]^{1/(q-1)}}{Z_q}$$

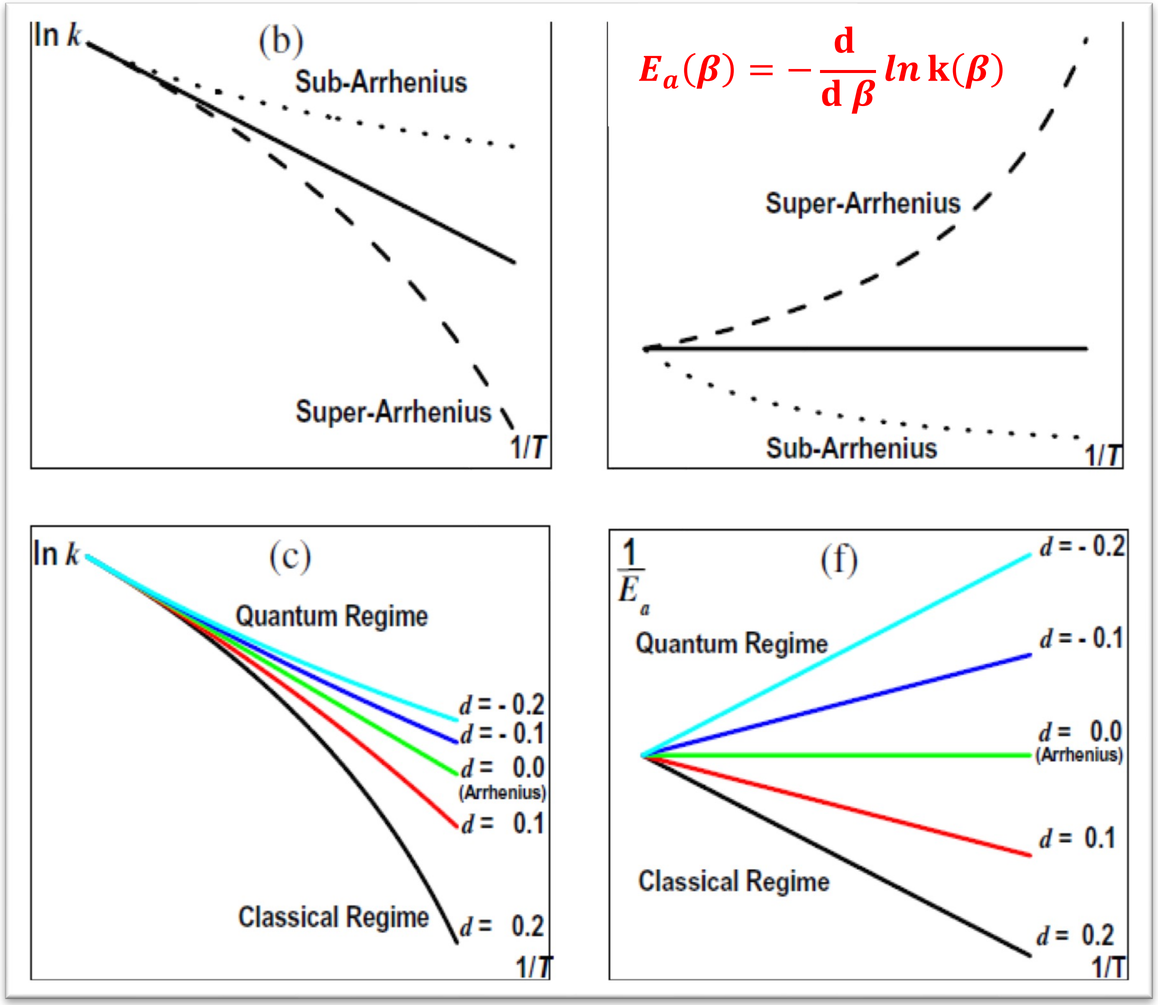
C. Tsallis, J Stat Phys **52**, 479 (1988)

Deformed-Arrhenius law
(d -Arrhenius)

$$\boxed{d = q - 1}$$

$$k(T) \equiv A\left[1 - d\,\frac{\varepsilon^{\ddagger}}{RT}\right]^{1/d}$$

V. Aquilanti, *et al*, Chem Phys Lett 498, 209 (2010)



Frequency for crossing the barrier

sub-Arrhenius $$d = -\frac{1}{3}\left(\frac{h\nu^{\ddagger}}{2\varepsilon^{\ddagger}}\right)^2$$

Barrier

V. H. Carvalho-Silva, *et al*, Chem Phys Lett **590**, 201 (2013)

Statistical Thermodynamics

➢ **Thermodynamic limit.** magnitude of Avogadro number $\mathcal{O}(10^{24})$

Studien über das Gleichgewicht der lebendigen Kraft zwischen bewegten materiellen Punkten.[1])

(Wien. Ber. 58. S. 517—560. 1868.)

$$\boxed{\frac{1}{\varkappa}\left(1-\frac{k}{n\varkappa}\right)^n dk = \frac{1}{\varkappa}\cdot e^{-\frac{k}{\varkappa}} dk.}$$

Boltzmann (1868)

XCIV. *On Boltzmann's Theorem on the average distribution of energy in a system of material points.*

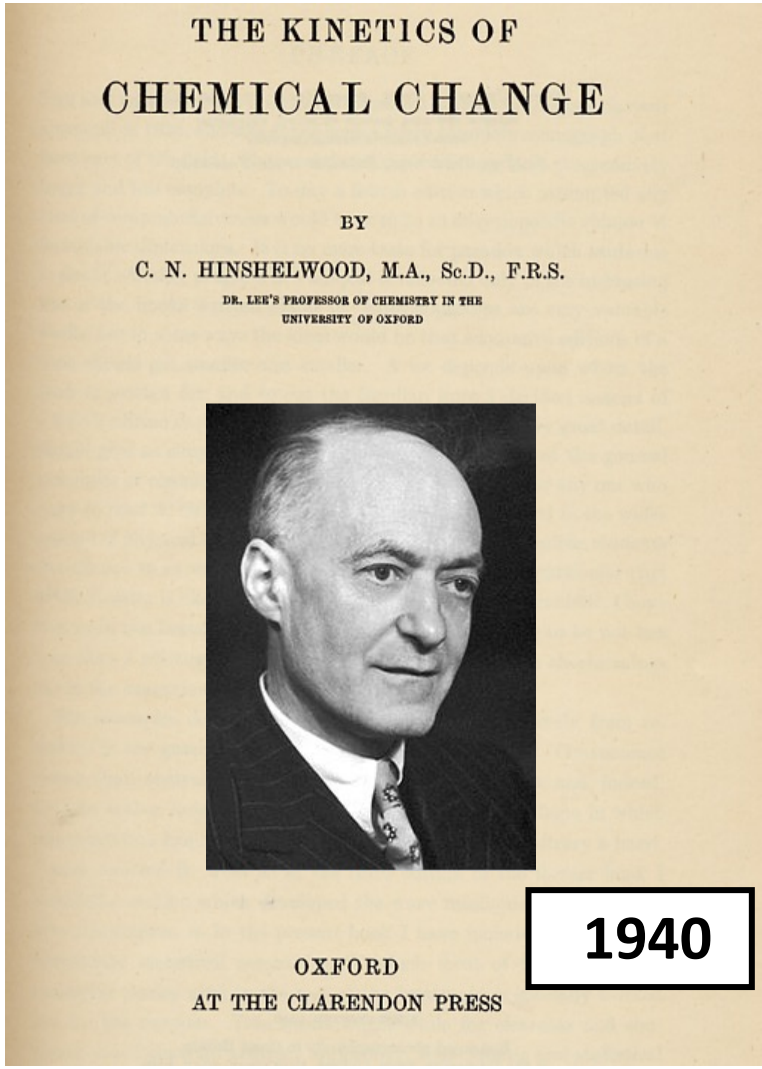
[From the *Cambridge Philosophical Society's Transactions*, Vol. XII.]

$$\boxed{\frac{\Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{1}{2}\right)\Gamma\left(\frac{n-1}{2}\right)} \frac{[E-V-k_n]^{\frac{n-3}{2}}}{[E-V]^{\frac{n-2}{2}}} k_n^{-\frac{1}{2}} dk_n}$$

$$\boxed{\frac{1}{\sqrt{2\pi}}\frac{1}{K} e^{-\frac{k}{2K}} dk}$$

Maxwell (1879)

Chemical Kinetics


THE KINETICS OF

CHEMICAL CHANGE

BY

C. N. HINSHELWOOD, M.A., Sc.D., F.R.S.

DR. LEE'S PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF OXFORD

1940

OXFORD

AT THE CLARENDON PRESS

Nobel in Chemistry 1956

A molecule may, in a given collision, gain or lose energy. Let us call one in which it **gains** energy, **favourable** and one in which it **loses** energy, **unfavourable**. To accumulate energy much in excess of the average the molecule may be supposed to need a lucky run of favourable collisions. In a given collision let the chance of spoiling a favourable run be $\mathbf{1/X}$. Then the chance of continuing it will be $\mathbf{(1-1/X)}$. The chance that the run continues for $\mathbf{Z}$ collisions is therefore

$$\left(1-\frac{1}{X}\right)^{Z} = \left(1-\frac{1}{X}\right)^{-\left(\frac{Z}{X}\right)(-X)} \xrightarrow{-X=n} \boxed{\left[\left(1+\frac{1}{n}\right)^{n}\right]}^{-\frac{Z}{X}}$$

Euler's limit of the exponential function

Chemical Kinetics

The Theory of

RATE PROCESSES

The Kinetics of Chemical Reactions, Viscosity, Diffusion and Electrochemical Phenomena

by SAMUEL GLASSTONE

KEITH J. LAIDLER

Associate Professor of Chemistry, Catholic University of America, Washington, D. C.

and HENRY EYRING, PH.D.

Dean of the Graduate School and Professor of Chemistry, University of Utah

PRINCETON, N.J.,
May, 1941.

INTERNATIONAL STUDENT EDITION

1941

McGRAW-HILL BOOK COMPANY, INC.

NEW YORK AND LONDON

Particles as Thermometer.†—It is necessary to consider next a box containing N particles, each of which has energy of translation in three degrees of freedom. Since each particle requires three quantum numbers for its complete description, the N particles‡ will require $3N$ quantum numbers. The number of states for which the total translational energy lies between zero and E is thus proportional to $E^{\frac{3}{2}N}$. Let the particles under consideration be N noninteracting molecules, and suppose an additional molecule is added to the box. If the total energy of the $N + 1$ molecules is W, then the probability $P(w)$ that the precise amount of energy w shall be uniquely in the extra molecule is simply equal to the probability that the remaining N molecules shall have energy $W - w$ in $3N$ degrees of freedom.

$$P(w) = \text{const.} \times g\left(1 - \frac{w}{W}\right)^{\frac{3}{2}N-1}$$

An Elementary Formulation of Statistical Mechanics

HENRY EYRING and JOHN WALTER
Princeton University, Princeton, New Jersey

1941

Cite This: *J. Chem. Educ.* 1941, 18, 2, 73
Publication Date: February 1, 1941
https://doi.org/10.1021/ed018p73

$$P(\epsilon) = a\left(1 - \frac{\epsilon}{sE_{av.}}\right)^{s-1}$$
$$= a\left\{1 - \frac{(s-1)}{s}\left(\frac{\epsilon}{E_{av.}}\right) + \frac{(s-1)(s-2)}{2!s^2}\left(\frac{\epsilon}{E_{av.}}\right)^2 - \frac{(s-1)(s-2)(s-3)}{3!s^3}\left(\frac{\epsilon}{E_{av.}}\right)^3 + \ldots\right\}$$

Avoiding the Thermodynamic Limit

Thermodynamic limit

$$\boldsymbol{V \to \infty;\ N \to \infty;\quad N/V = finite}$$

Magnitude of Avogadro number $\mathcal{O}(10^{24})$

A. [illegible], I[illegible]B (2014).
C. [illegible], E[illegible] [illegible]-E[illegible] [illegible], 2008).

$$\lim_{\forall\beta;\ d\to 0} A\left(1 - d\varepsilon^{\ddagger}\beta\right)^{1/d} = A\, e^{-\varepsilon^{\ddagger}\beta}$$

Kinetic limit

$$i)\quad \beta \to \mathbf{0};\ d = \frac{\varepsilon^{\dagger}}{\varepsilon^{\ddagger}} = \boldsymbol{finite}$$

$$ii)\quad \beta \to \infty;\ d\varepsilon^{\ddagger}\beta \to \mathbf{1}$$

Magnitude of Eyring number $\mathcal{O}(10^{13})$

[illegible] H. C[illegible]-[illegible], [illegible] D. C[illegible], [illegible] A[illegible], [illegible]25, 2098 (2020).
[illegible] A[illegible], [illegible], [illegible]F[illegible]28, 787 (2018).
[illegible] B[illegible], [illegible], E[illegible]16, 6497 (2014).

$$\lim_{\forall d;\ \beta\to 0} A\left(1 - d\varepsilon^{\ddagger}\beta\right)^{1/d} = A\, e^{-\varepsilon^{\ddagger}\beta}$$

$$\lim_{\forall d;\ d\varepsilon^{\ddagger}\beta\to 1} A\left(1 - d\varepsilon^{\ddagger}\beta\right)^{1/d} = \begin{cases} 0 & (super) \\ A\,\beta^{1/d} & (sub) \end{cases}$$

Content

1. Scaled Rate Processes
2. **Renormalized differential equation – Transitivity**
3. Applications

The Scaling of Relaxation Processes

PHYSICAL REVIEW B VOLUME 32, NUMBER 1 1 JULY 1985

Critical slowing down in spin glasses and other glasses: Fulcher versus power law

J. Souletie and J. L. Tholence
Centre de Recherches sur les Très Basses Températures, Centre National de la Recherche Scientifique, Boîte Postale 166 X, 38042 Grenoble-Cédex, France

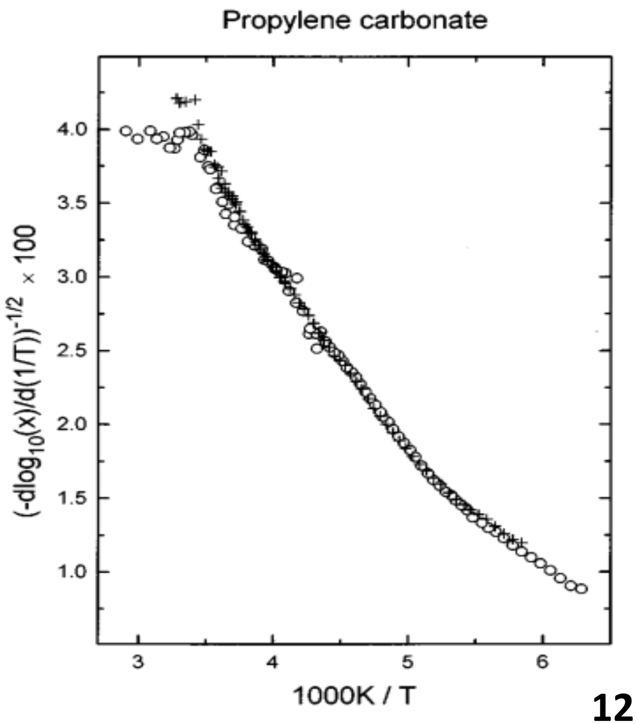
(Received 20 February 1985)

$$\tau = \tau_0 \exp[E_a/k(T-T_0)]$$

$$\tau = \tau^* \left(\frac{T}{T-T^*} \right)^{z\nu}$$

$$\mathcal{F} = \left(\frac{dT_g(f)}{d\ln f} \right)^{1/2} = \frac{T_g(f) - T_0}{\sqrt{E_a/k}} ,$$

$$\mathcal{P} = \frac{d\ln T_g(f)}{d\ln f} = \frac{T_g(f) - T^*}{z\nu T^*} \sim \frac{\mathcal{F}^2}{T_g(f)} ,$$



Dynamics of glass-forming liquids. II. Detailed comparison of dielectric relaxation, dc-conductivity, and viscosity data

J. Chem. Phys. **104**, 2043 (1996); https://doi.org/10.1063/1.470961

F. Stickel, E. W. Fischer, *and* R. Richert

Renormalization Group

PHYSICAL REVIEW B VOLUME 4, NUMBER 9 1 NOVEMBER 1971

Renormalization Group and Critical Phenomena.
I. Renormalization Group and the Kadanoff Scaling Picture*

Kenneth G. Wilson
Laboratory of Nuclear Studies, Cornell University, Ithaca, New York 14850
(Received 2 June 1971)

The Kadanoff theory of scaling near the critical point for an Ising ferromagnet is cast in differential form. The resulting differential equations are an example of the differential equations of the renormalization group. It is shown that the Widom-Kadanoff scaling laws arise naturally from these differential equations if the coefficients in the equations are analytic at the critical point. A generalization of the Kadanoff scaling picture involving an "irrelevant" variable is considered; in this case the scaling laws result from the renormalization-group equations only if the solution of the equations goes asymptotically to a fixed point.

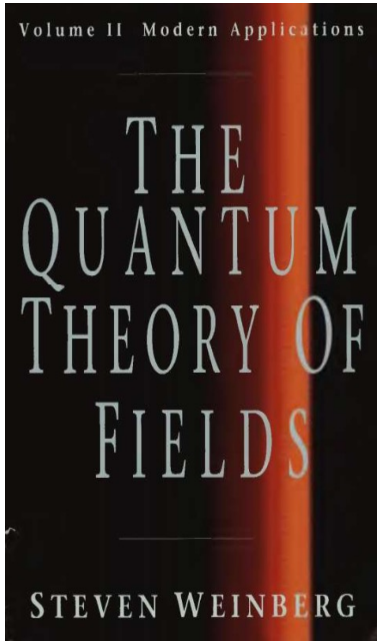
Equations (9) and (10) are the renormalization-group equations suggested by the Kadanoff block picture. Because of the questionable validity of

$$\xi(K, h) = L\xi(K_L, h_L). \tag{5}$$

$$\frac{dK_L}{dL} = \frac{1}{L} u(K_L, h_L{}^2). \tag{9}$$

$$\frac{dK_L}{dL} \simeq \frac{1}{L}(K_L - K_c)y\ , \tag{15}$$

$$y = \frac{\partial u}{\partial K}(K_c, 0)\ , \tag{17}$$



"Beta plane"

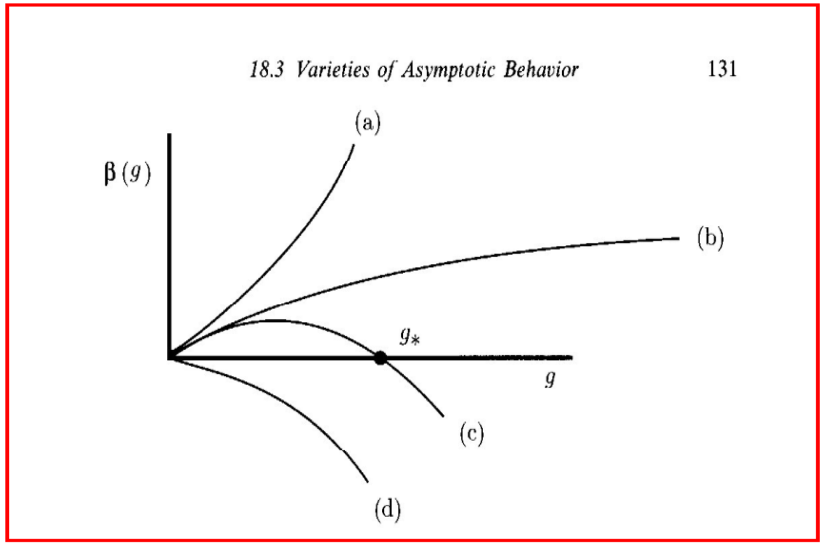


Figure 18.4. Schematic representation of four possible forms of the function $\beta(g)$. For such forms of $\beta(g)$, the running coupling g_μ would: (a) approach infinity at a finite value of μ; (b) continue to grow as μ increases; (c) approach a finite limit g_* for $\mu \to \infty$; (d) approach zero for $\mu \to \infty$.

equation becomes simply

$$\mu \frac{d}{d\mu} g_\mu = \beta(g_\mu, 0) \equiv \beta(g_\mu)\,, \tag{18.2.9}$$

which is often known as the *Callan–Symanzik equation.*[1] We are to cal-

A Scaling Formulation – Transitivity Function

$$\beta = \frac{1}{kT}$$

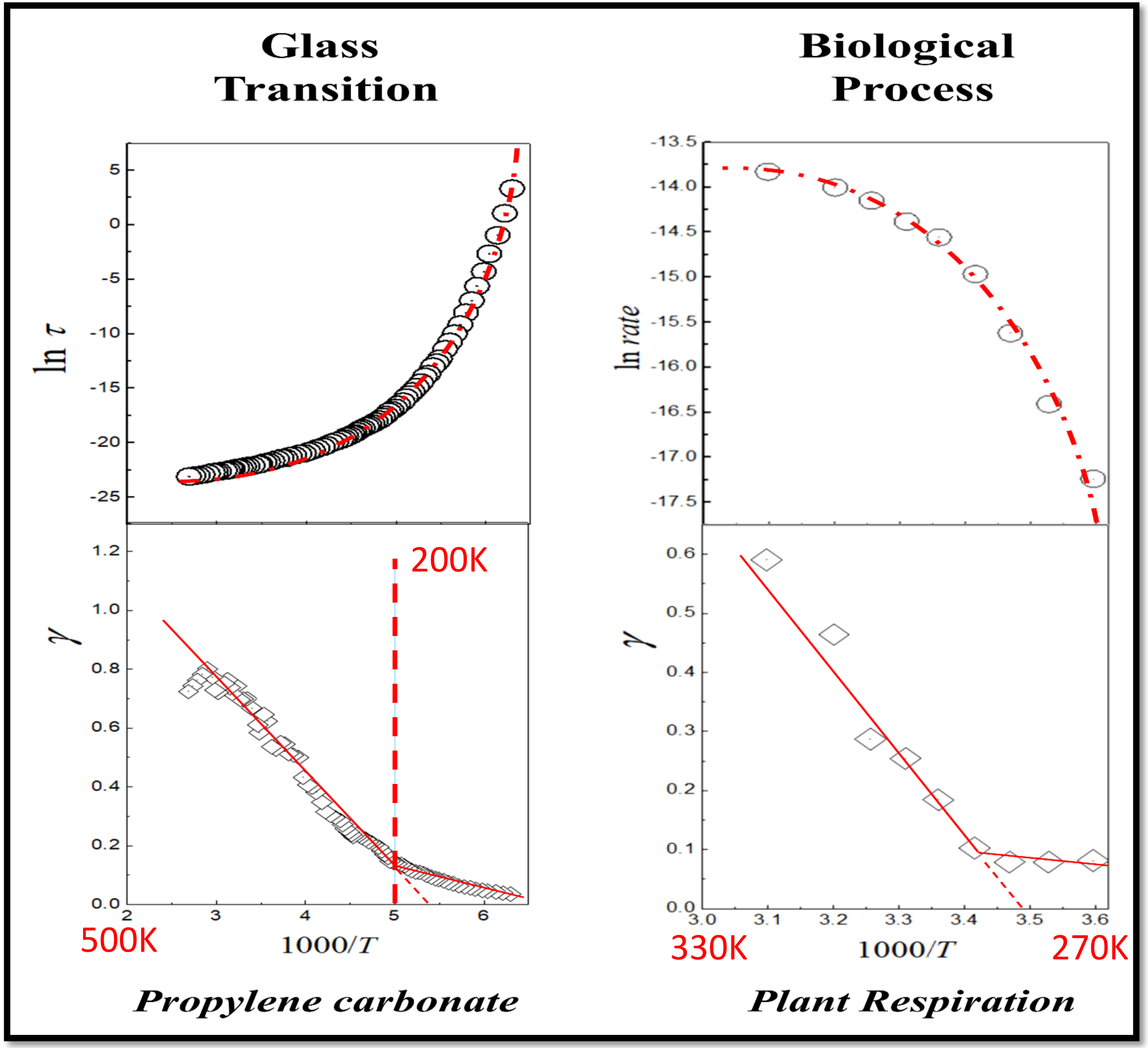
$$E_a = -\frac{d \ln k(\beta)}{d\beta} = -\frac{1}{k(\beta)}\frac{dk(\beta)}{d\beta}.$$

$$\gamma(\beta) \equiv \frac{1}{E_a(T)}. \qquad \gamma(\beta) = \sum_{n=-\infty}^{\infty} C_n(\beta - \beta_0)^n,$$

$$\gamma(\beta) \equiv \frac{1}{E_a} = \underbrace{\frac{1}{E} - d\beta}_{\text{The linearized equation}} + O(\beta^2),$$

$$\boxed{k(\beta) = A(1 - dE\beta)^{1/d},}$$

Aquilanti, Coutinho, Carvalho-Silva, Philos Trans R Soc Lond A 375, 20160204 (2017)

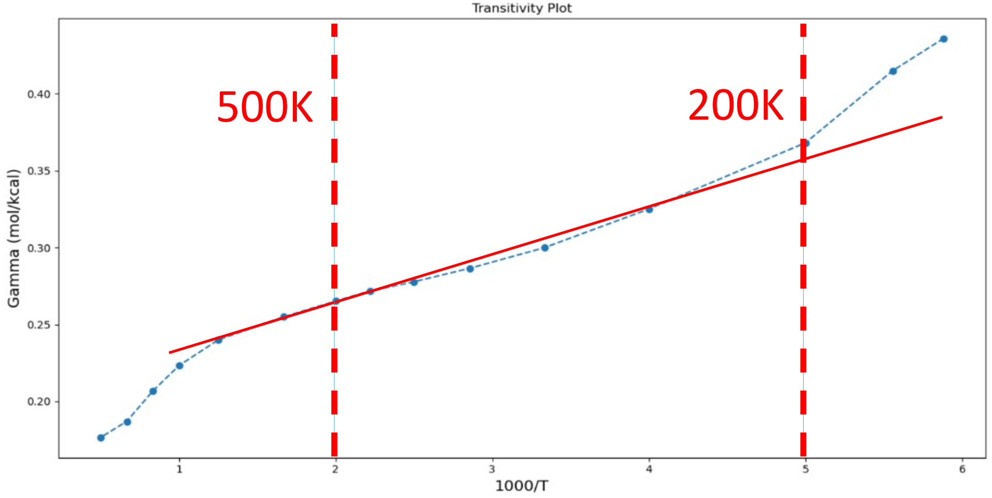


A Scaling Formulation – Transitivity Function

VOLUME 91, NUMBER 6 PHYSICAL REVIEW LETTERS week ending 8 AUGUST 2003

H + H_2 Thermal Reaction: A Convergence of Theory and Experiment

Steven L. Mielke,[1] Kirk A. Peterson,[1,2] David W. Schwenke,[3] Bruce C. Garrett,[1] Donald G. Truhlar,[4] Joe V. Michael,[5] Meng-Chih Su,[5] and James W. Sutherland[5]



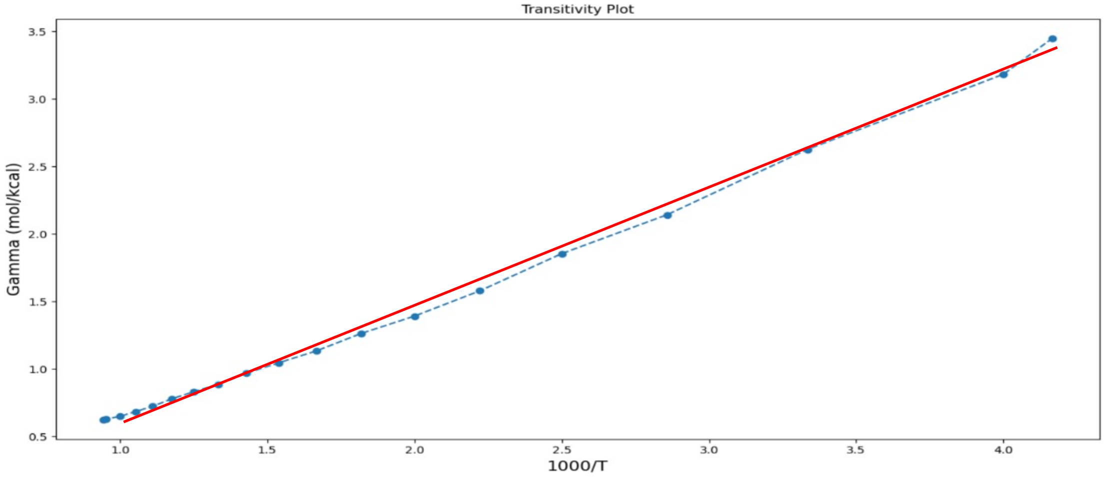
INTERNATIONAL JOURNAL OF CHEMICAL KINETICS

Volume 17, Issue 12
December 1985
Pages 1281-1297

Article

Kinetic study of the reaction of OH with HCl from 240–1055 K

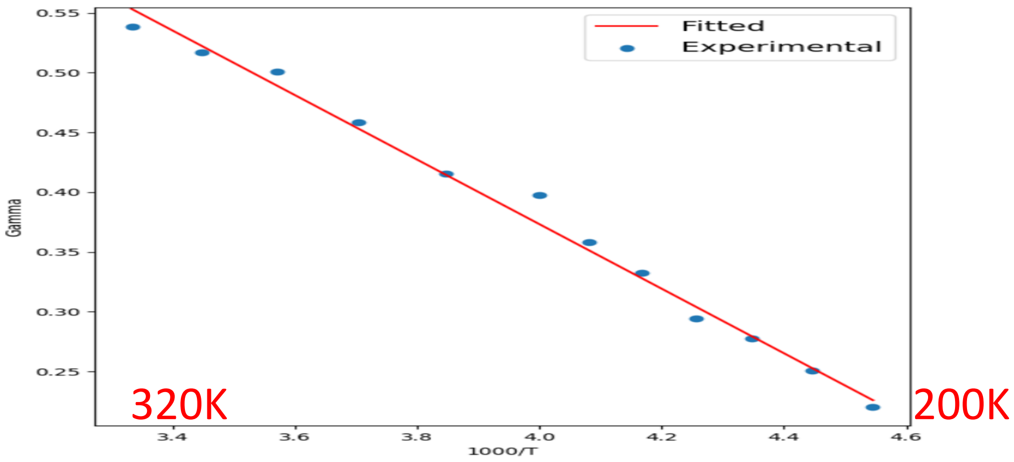
A. R. Ravishankara, P. H. Wine, J. R. Wells, R. L. Thompson

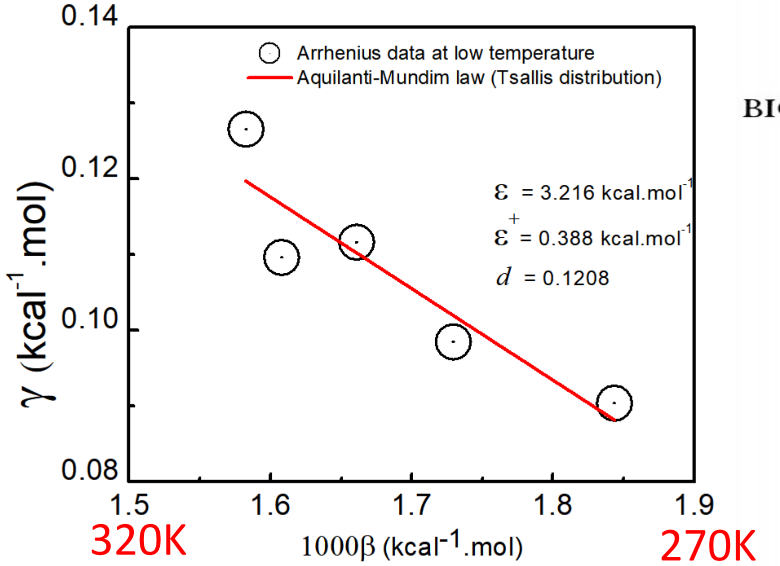


Dynamical aspects of supercooled TIP3P-water in the grooves of DNA

J. Chem. Phys. 150, 235101 (2019); https://doi.org/10.1063/1.5100601

M. A. F. dos Santos[1], M. A. Habitzreuter[1], M. H. Schwade[1], R. Borrasca[1], M. Antonacci[1], G. K. Gonzatti[2], P. A. Netz[2], and M. C. Barbosa[3,a)]





QUANTITATIVE LAWS

IN

BIOLOGICAL CHEMISTRY

BY

SVANTE ARRHENIUS

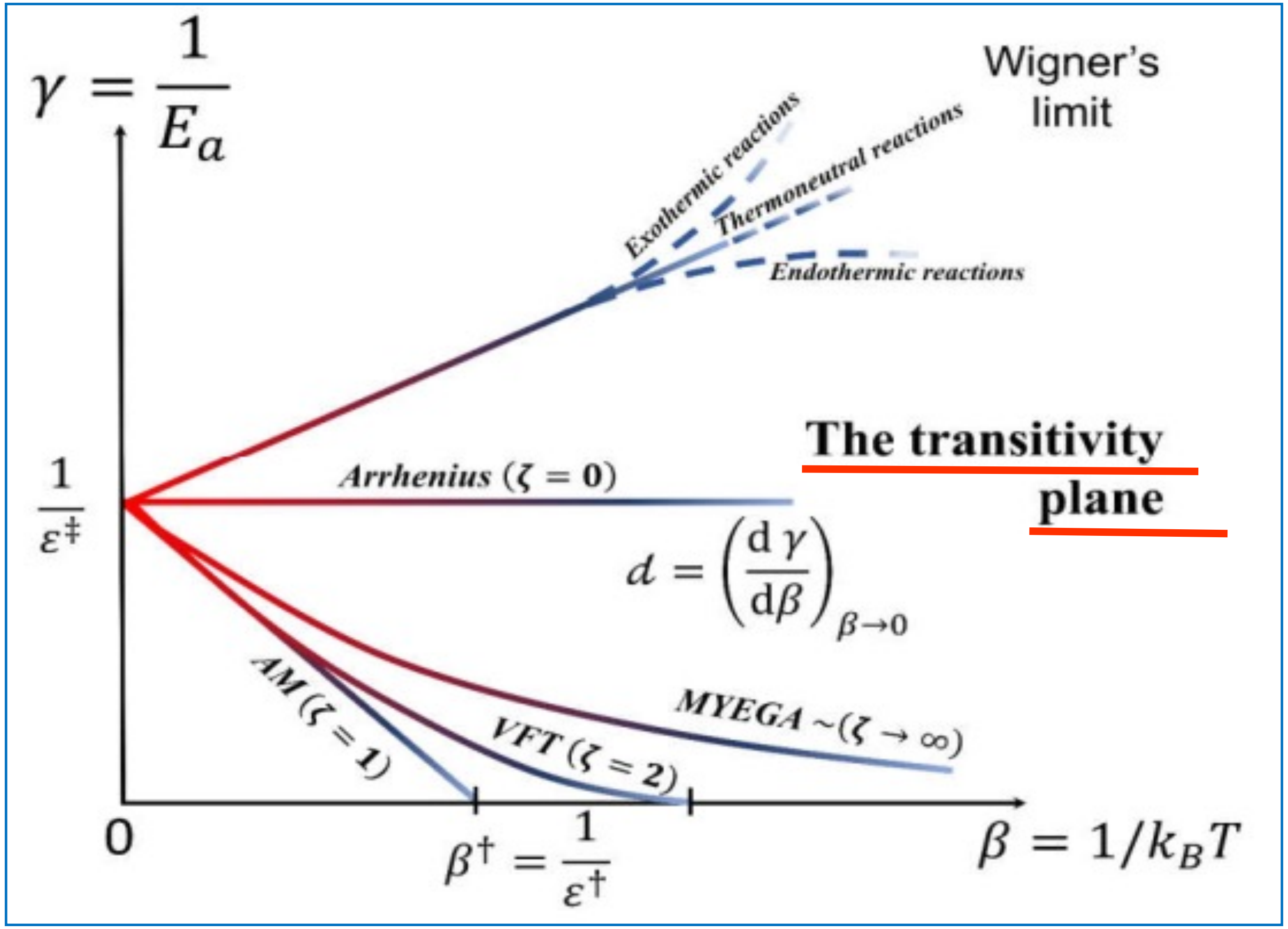
PH.D., M.D., LL.D., F.R.S.

NOBEL LAUREATE

DIRECTOR OF THE NOBEL INSTITUTE OF PHYSICAL CHEMISTRY

LONDON
G. BELL AND SONS, LTD.
1915

Universality Classes in Rate Processes



Universality Classes

$$\boldsymbol{\gamma(\beta;\zeta) = \frac{1}{\varepsilon^\ddagger}\left(1 - \varepsilon^\dagger \beta\right)^{\zeta}}$$

$\zeta = 0$ *Arrhenius (Boltzmann)*

$\zeta = 1$ *Deformed-Arrhenius (Tsallis)*

$\zeta = 2$ *Vogel-Fulcher-Tammann (VFT)*

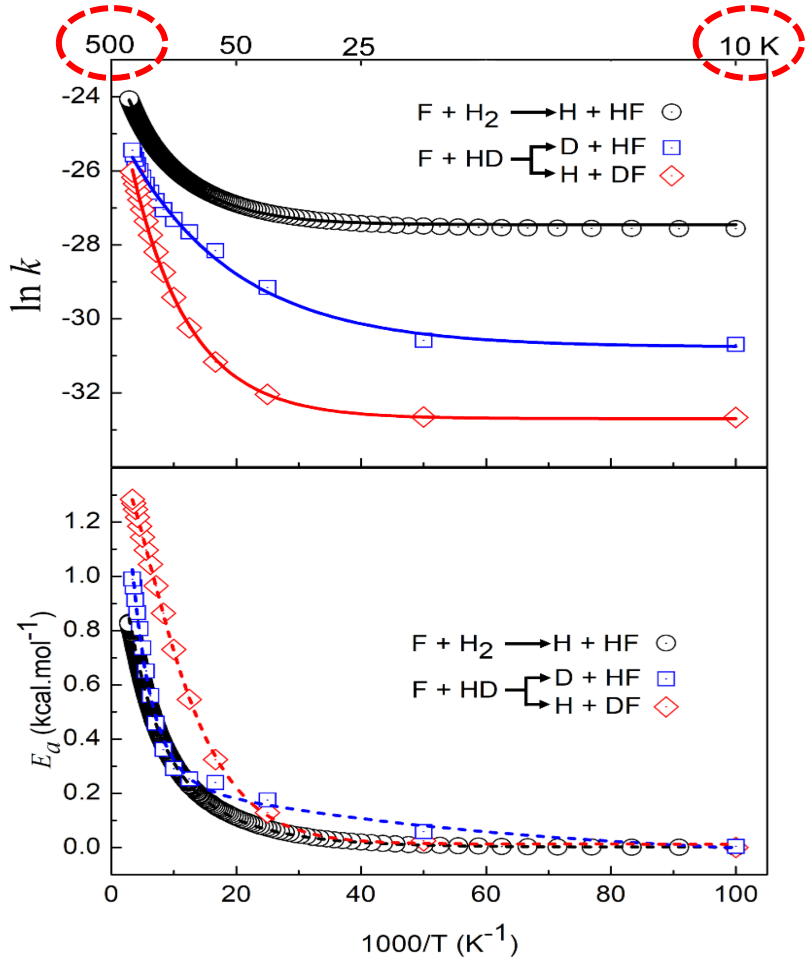
ζ *Universality class exponent*

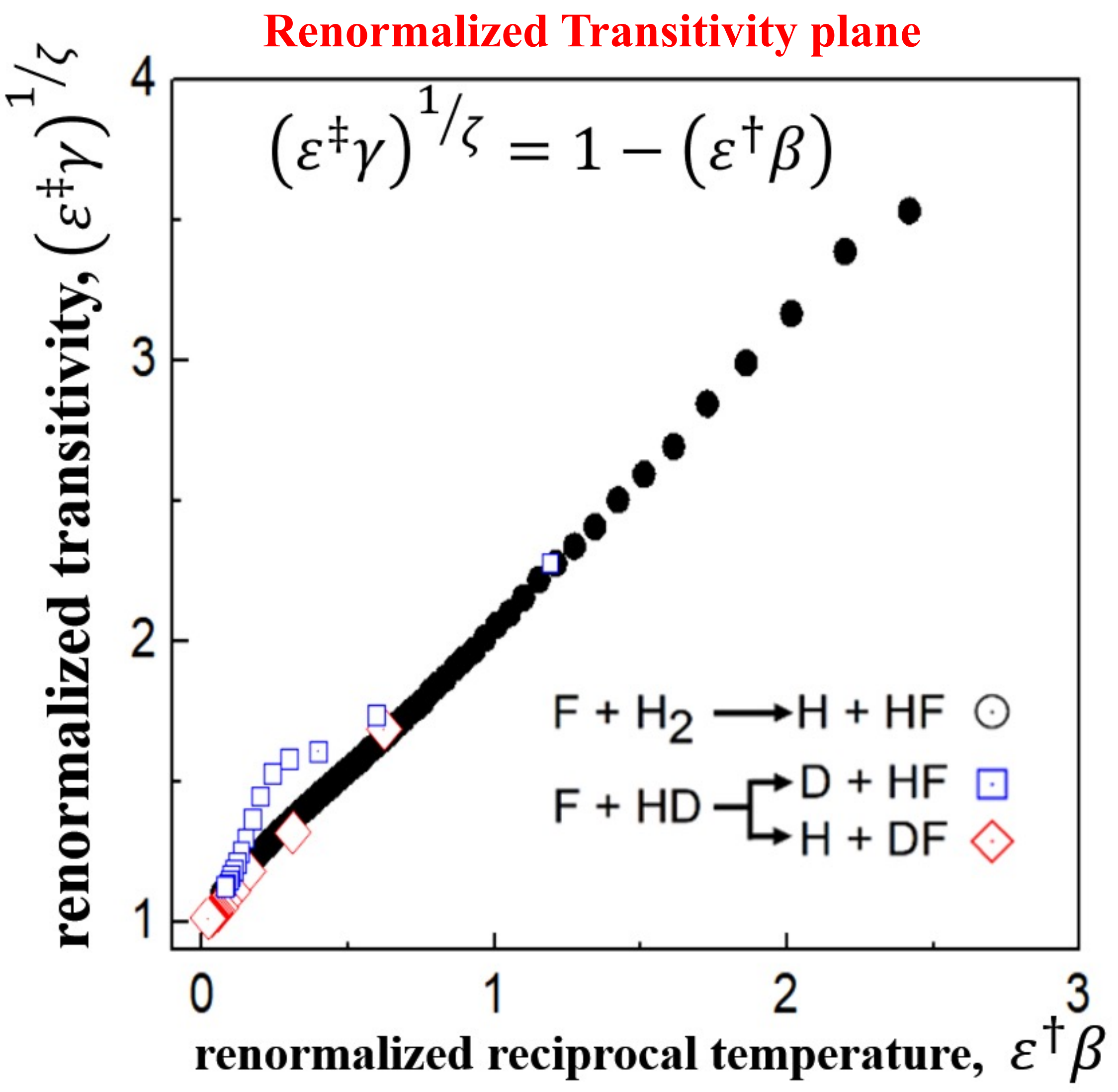
V. H. Carvalho-Silva, N. D. Coutinho, and V. Aquilanti, Molecules 25, 2098 (2020).
V. H. Carvalho-Silva, N. D. Coutinho, and V. Aquilanti, Front Chem 7, 380 (2019).

A Scaling Formulation – Transitivity Function

$$\gamma(\beta;\zeta) = \frac{1}{\varepsilon^{\ddagger}}\left(1 - \varepsilon^{\dagger}\beta\right)^{\zeta}$$

$$\boxed{k(\beta;\zeta) = A \exp\left[-\frac{1}{(\zeta-1)}\frac{\varepsilon^{\ddagger}}{\varepsilon^{\dagger}}\left(1-\varepsilon^{\dagger}\beta\right)^{1-\zeta}\right],}$$





V. H. Carvalho-Silva, *et al*, Rend Lincei Sci Fis Nat (2023). *Accepted*
D. De Fazio, V. Aquilanti, and S. Cavalli, Front Chem 7, 328 (2019)

Content

1. Scaled Rate Processes
2. Renormalized differential equation – Transitivity
3. **Applications**

Sub-Arrhenius

Journal of COMPUTATIONAL CHEMISTRY
Volume 38, Issue 3
January 30, 2017
Pages 178-188

Deformed transition-state theory: Deviation from Arrhenius behavior and application to bimolecular hydrogen transfer reaction rates in the tunneling regime

Valter H. Carvalho-Silva, Vincenzo Aquilanti, Heibbe C. B. de Oliveira, Kleber C. Mundim

$$k_{d-TST}(T) = \frac{kT}{h}\frac{Q^{TS}(T)}{Q_{\mathrm{Reactants}}(T)}\left(1 - d\frac{E}{kT}\right)^{\frac{1}{d}}$$

$$d = -\frac{1}{3}\left(\frac{h\nu^{\ddagger}}{2\varepsilon^{\ddagger}}\right)^{2}$$

2016

THE JOURNAL OF PHYSICAL CHEMISTRY A
Article
pubs.acs.org/JPCA

Investigation of the Abstraction and Dissociation Mechanism in the Nitrogen Trifluoride Channels: Combined Post-Hartree–Fock and Transition State Theory Approaches

D. Claudino,[†] R. Gargano,[‡] Valter H. Carvalho-Silva,[§] Geraldo M. e Silva,[‡] and W. F. da Cunha*[,†,‡]

2016

THE JOURNAL OF PHYSICAL CHEMISTRY C
Article
pubs.acs.org/JPCC

Methanol Solvation Effect on the Proton Rearrangement of Curcumin's Enol Forms: An *Ab Initio* Molecular Dynamics and Electronic Structure Viewpoint

Lauriane G. Santin,[†,‡] Eduardo M. Toledo,[†] Valter H. Carvalho-Silva,*[,†] Ademir J. Camargo,[†] Ricardo Gargano,[‡] and Solemar S. Oliveira*[,†]

2017

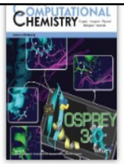
PCCP
ROYAL SOCIETY OF CHEMISTRY
PAPER
Check for updates
Cite this: *Phys. Chem. Chem. Phys.*, 2017, 19, 24467

A novel assessment of the role of the methyl radical and water formation channel in the CH_3OH + H reaction†

Flávio O. Sanches-Neto,[a] Nayara D. Coutinho*[b] and Valter H. Carvalho-Silva *[a]

2018

Journal of COMPUTATIONAL CHEMISTRY
Volume 39, Issue 30
November 15, 2018
Pages 2508-2516



Related
Information

Full Paper

Kinetics of the OH+HCl→H_2O+Cl reaction: Rate determining roles of stereodynamics and roaming and of quantum tunneling

Nayara D. Coutinho, Flavio O. Sanches-Neto, Valter H. Carvalho-Silva, Heibbe C. B. de Oliveira, Luiz A. Ribeiro, Vincenzo Aquilanti

Molecules 24, (**2019**).
Struct Chem 31, 609 (**2020**).
PCCP 23, 6738 (**2021**).
Chemosphere 278, 130401 (**2021**).
Environ Sci Technol 55, 12437 (**2021**).
Atmos Environ 275, 119019 (**2022**).
Proc Saf Environ Prot 166, 478 (**2022**).
RSC Adv 12, 34746 (**2022**).
Chemosphere 324, 138278 (**2023**).
J Braz Chem Soc 34,1119 (**2023**).

super-Arrhenius

Super-Arrhenius Temperature Dependence of Transport Properties for Ultraslow Glass-Forming Liquids: Transitivity Plots Unveiling Classes of Universality

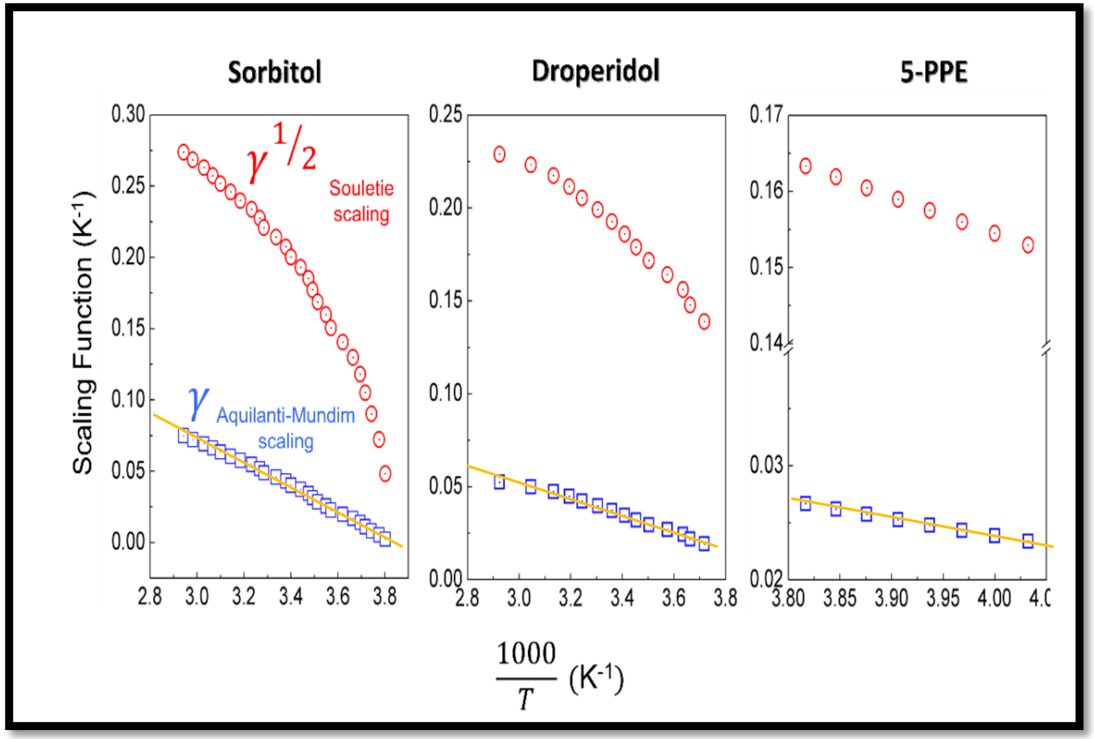
V.H. Carvalho-Silva; N.D. Coutinho; V. Aquilanti; **Unpublished**

$$\chi(T) = \chi_0 \, exp\left(\frac{\boldsymbol{E_{VFT}}}{R(T - \boldsymbol{T_0})}\right)$$

VFT

$$\chi(T) = \chi_0 \left(1 - \frac{\boldsymbol{T^{\dagger}}}{T}\right)^{-\varepsilon^{\ddagger}/RT^{\dagger}}$$

d-Arrhenius

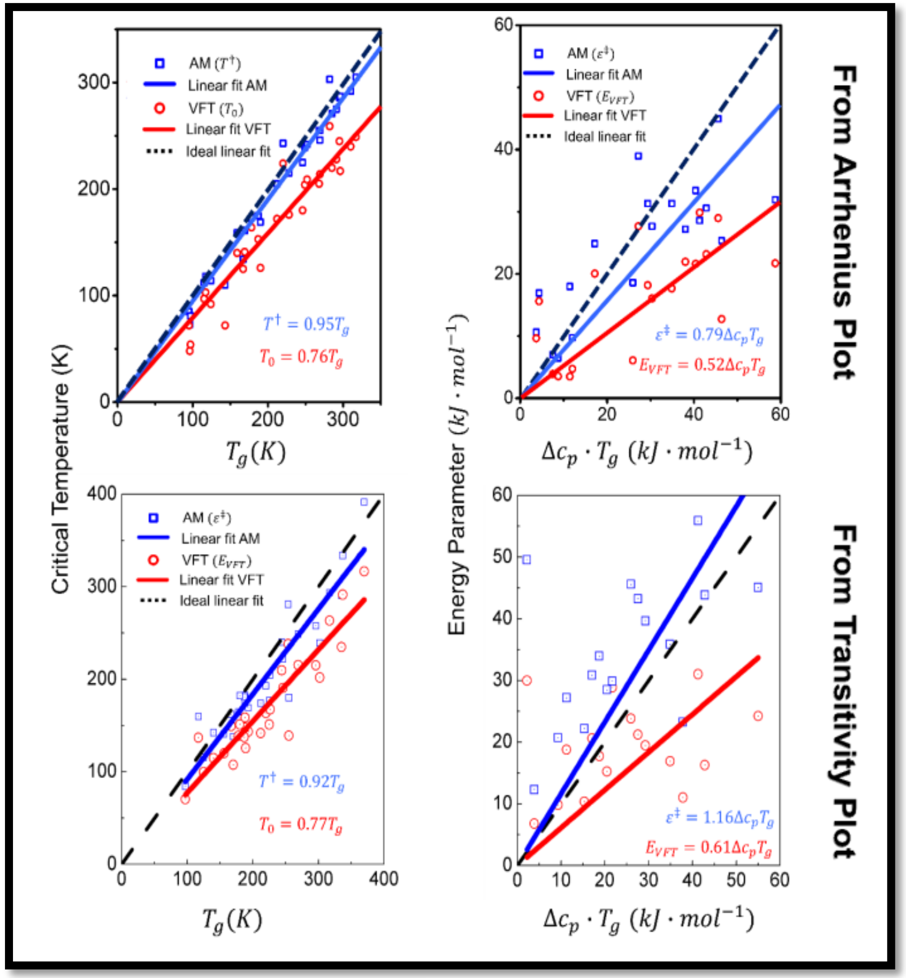


$T^{\dagger} = 0.92T_g$

$T_0 = 0.77T_g$

$\varepsilon^{\ddagger} = 1.16\Delta c_p T_g$

$E_{VFT} = 0.61\Delta c_p T_g$



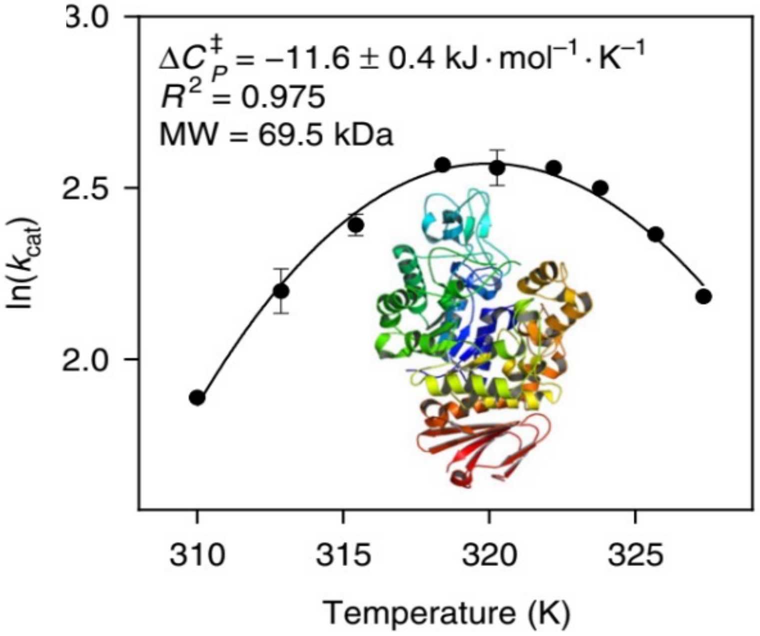
$$\chi = \chi_0 \left(1 - \frac{T_g}{T}\right)^{-\Delta c_p / R}$$

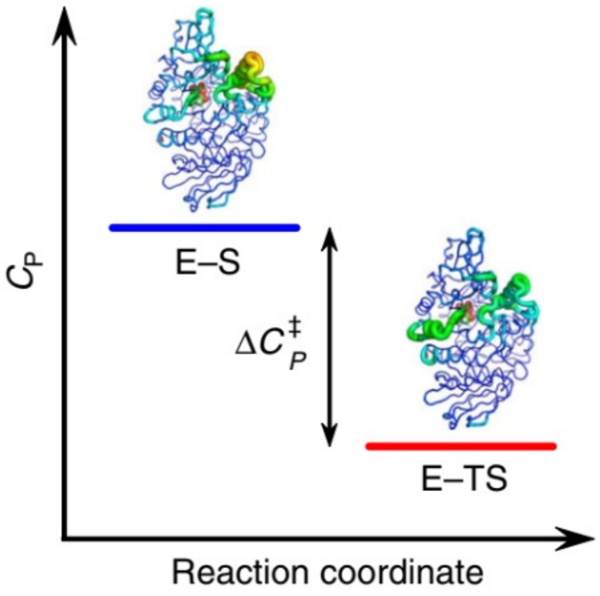
$$d = q - 1 = R/\Delta c_p$$

Rise and Decline in Arrhenius plot

Macromolecular Rate Theory (MRT)

M. W. van der Kamp, *et al*, Nat Commun 9, 1177 (2018).





Constant

$$ln\,k(T) = ln\left(\frac{1}{h\beta}\right) - \left[\Delta H_0^{\ddagger} + \frac{\Delta C_p^{\ddagger}}{\mathbf{R}}\left(\frac{1}{\beta} - \frac{1}{\beta_0}\right)\right]\beta + \left[\frac{\Delta S_0^{\ddagger}}{\mathbf{R}} + \frac{\Delta C_p^{\ddagger}}{\mathbf{R}}\,ln\left(\frac{\beta_0}{\beta}\right)\right]$$

PNAS RESEARCH ARTICLE | ECOLOGY 2022 Vol. 119 No. 30 e2119872119

A general theory for temperature dependence in biology

José Ignacio Arroyo[a,b,1,2], Beatriz Díez[c,d,e], Christopher P. Kempes[b], Geoffrey B. West[b], and Pablo A. Marquet[a,b,f,g,h,1,2]

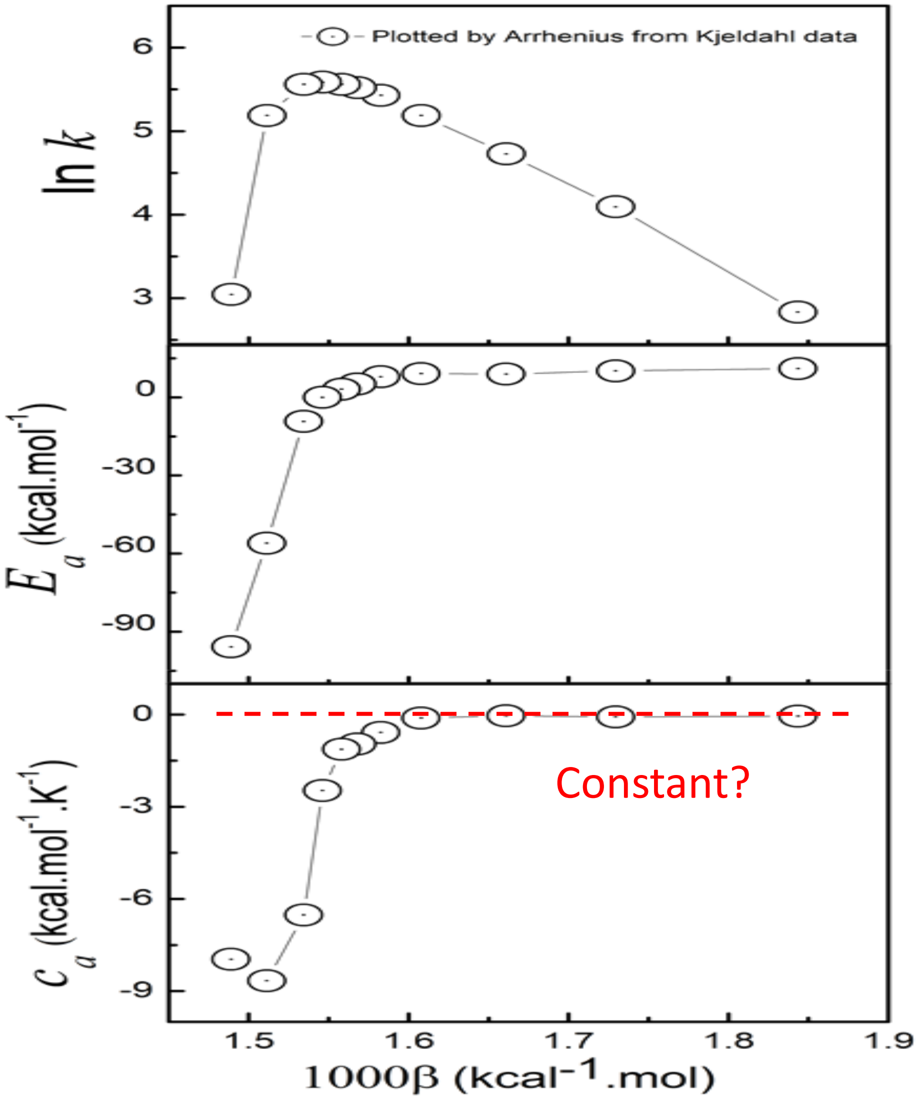
Contributed by Pablo Marquet; received October 31, 2021; accepted April 7, 2022; reviewed by Raymond Huey and Andrea Rinaldo

$$k = \frac{k_B}{h} e^{\frac{\Delta S_0}{R}}\, T_0^{\frac{-\Delta C}{R}} \left(\frac{1}{T}\right)^{-\left(\frac{\Delta C}{R}+1\right)} e^{\frac{-\Delta H}{RT}}.$$

Constant

- **La Mer's Interpretation** V. K. La Mer, J Chem Phys 1, 289 (1933)

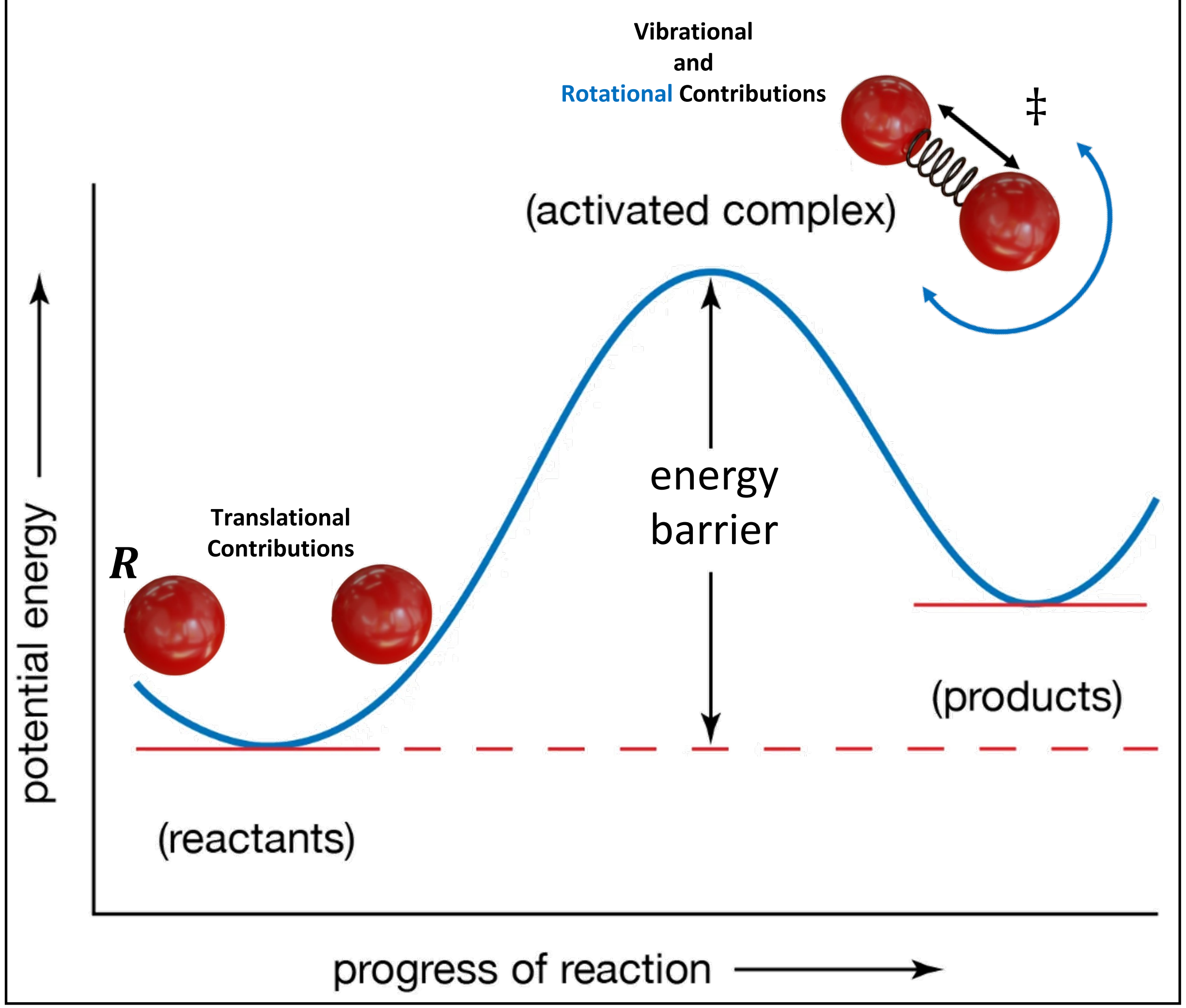
$$c_a = \frac{\mathrm{d}\,E_a}{\mathrm{d}\,T} = -k_B\beta^2\frac{\mathrm{d}\,E_a}{\mathrm{d}\,\beta} = k_B\beta^2\left(\frac{\mathrm{d}^2}{\mathrm{d}\,\beta^2}\ln k(\beta)\right)$$



Activation Heat Capacity

➢ **Perspectives – Expanding La Mer's Interpretation**

$$c_a \equiv k_B \beta^2 \left(-\frac{\mathrm{d}\,E_a}{\mathrm{d}\,\beta}\right) = c^{\ddagger} - \sum\nolimits_R c^R$$



$$c_a = c^{\ddagger} - \sum\nolimits_R c^R$$

Renormalized Differential Equations

$$-\frac{\mathrm{dt}}{\mathrm{d}\ln \mathrm{R}(t)} = \tau(\beta)[\mathrm{R(t)}]^{1-\rho}$$

$$-\frac{\mathrm{d}\,\beta}{\mathrm{d}\ln k(\beta)} = \gamma(\beta)$$

$$\frac{\gamma}{\beta}\frac{\mathrm{d}\;\ln\beta}{\mathrm{d}\ln\gamma} = \frac{R}{c_a}$$

Linearization

$$d = -\frac{1}{3}\left(\frac{(6k_B\theta_r)^2 - \left(h\nu^{\ddagger}/2\right)^2}{(\varepsilon^{\ddagger} + 6k_B\theta_r)^2}\right)$$

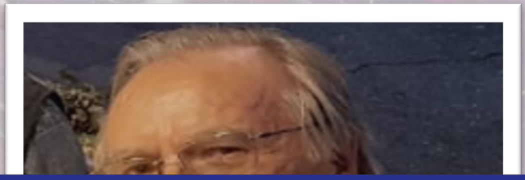
sub (d-TST)

$$d = -\frac{1}{3}\left(\frac{h\nu^{\ddagger}}{2\varepsilon^{\ddagger}}\right)^2$$

super

$$d = \frac{1}{3}\left(\frac{6k_B\theta_r}{\varepsilon^{\ddagger}}\right)^2$$

Acknowledgment



Evento do SQTEA em Pirenópolis-GO