LA-UR- 01-4420

LA-UR- 2001-

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Title: AN EXTENSION OF TRANSITION-STATE THEORY FOR SHOCK ENVIRONMENTS

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Submitted to: The Energetics Materials Review, Los Alamos National Laboratory, 6-9 August, 2001. This work was supported by the NW program office, JAMP program code.

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An extension of transition-state theory for shock environments‡

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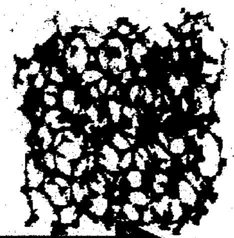
A qualitative chemical kinetics model is developed for shock environments based on a straight-forward extension of transition-state theory (TST). The model assumes that the distribution of initial velocities along a reaction coordinate is centered about the projection of the shock velocity along that coordinate. The resulting model possesses several highly desirable qualitative features. The first is an adiabatic quality in which there is a gaussian amplification of the reaction rate with projected-shock velocity relative to the thermal TST rate. The second is saturation of the amplification at a critical projected-shock velocity related to the barrier height of the reaction. Third is that the model can act as an extrapolation guide for extending thermally-measured rate constants to a shock environment. Finally, the explicit dependence of the reaction rate on projected-shock velocity, rather than the total shock speed, imparts a natural sense of anisotropy in the shock-induced kinetics. A 1D numerical simulation supports the presence of these features in shock-induced kinetics.

‡ Work supported by the US Department of Energy under contract W-7405-ENG-36 to the University of California.

An extension of transition-state theory for shock-induced chemical kinetics



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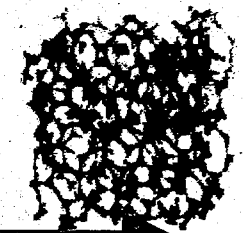
Acknowledgments
Jim Doll - Brown U, Lawrence Pratt - LANL
DOE Support - ASCI/NWP



Practical Chemical Kinetics

MOTIVATION

- Disagreements among exp'ts
- Anisotropy in single xtals
- Need for analytical modeling
- Transition-state theory (TST) is still king:

$$k_{TST} = \nu \exp(-E_a/k_B T)$$

T = temperature

E_a = activation energy

ν = vibrational frequency of reactant

ISSUES

- Thermal vs mechanical activation
- Hot spots
- Polymer degradation - anisotropy
- Poly-xtal vs single xtal

APPROACH

- TST can be"derived"
  - Approximate solution of Fokker-Planck eq.
  - Assume Boltzmann distributions
- Re-derive TST for nonBoltzmann distribution
- Check with numerical solutions

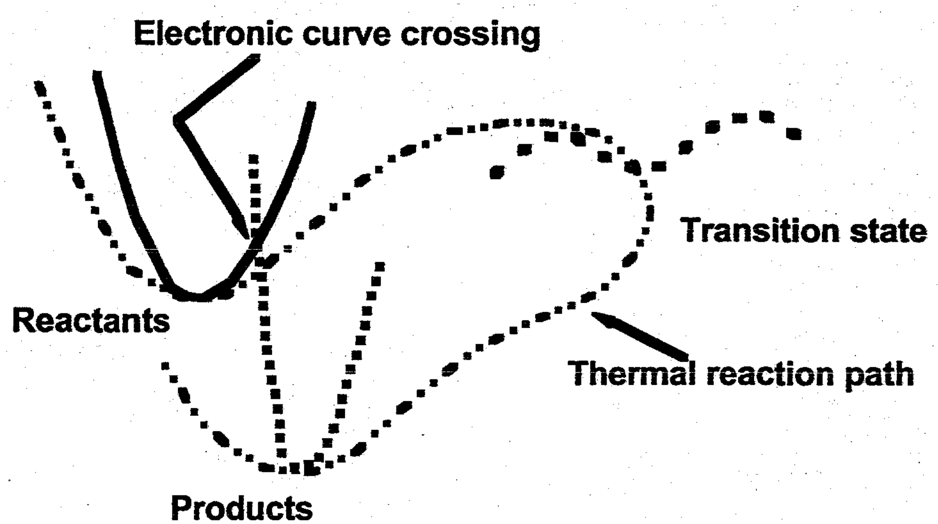
PROGRAMMMTIC CONNECTIONS

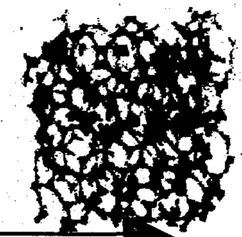
- HE detonation, initiation, hot spot modeling
- Relation of cook-off to detonation etc.
- Polymer degradation
- Constitutive models based on TST

Major Schools of Chemical Kinetics

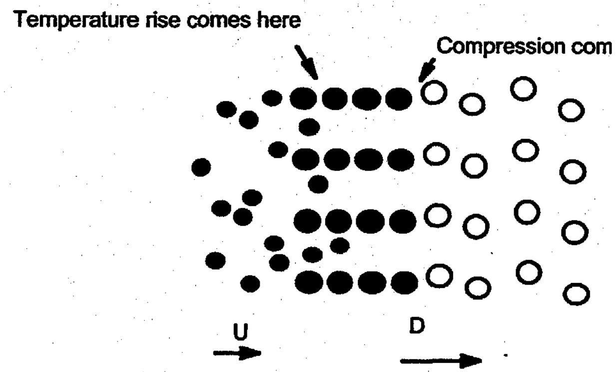
Thermally-based models

- Conventional TST: Arrhenius (1889) & Eyring (1935)
  - $k_{TST} = k_B T/h\ Q^{\ddagger}/(Q_A\ Q_B)\ \exp(-E_a/k_B T)$
- Starvation Kinetics: Eyring (1952)
  - $k_{TST} = k_{TST} * P(E_a/k_B T)$
- Activation volume: Eyring (1935)
  - $E_a \sim \Delta G^{\ddagger}$
- Curve-crossings - metal-insulator transitions: Gilman(1973)

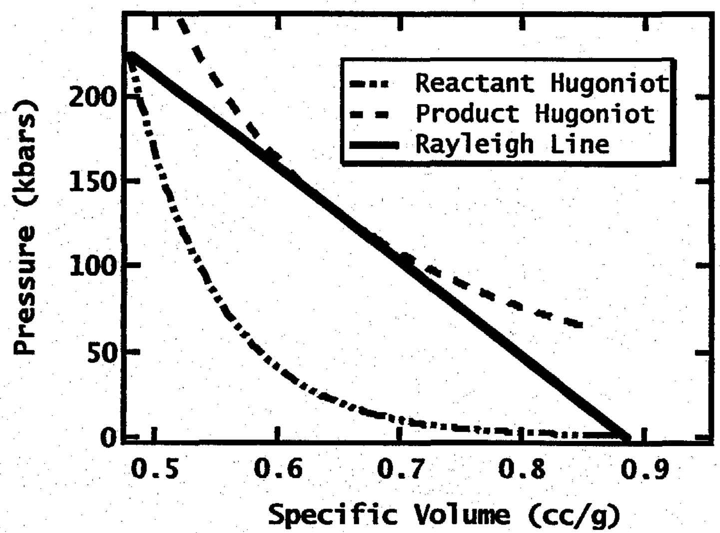




Shocked Materials Scenario



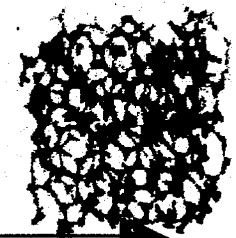
Three Main Zones in a Shock Front
Unreacted and equilibrated
Compressed and out of equilibrium
Product formation, returning to equilibrium and heat release

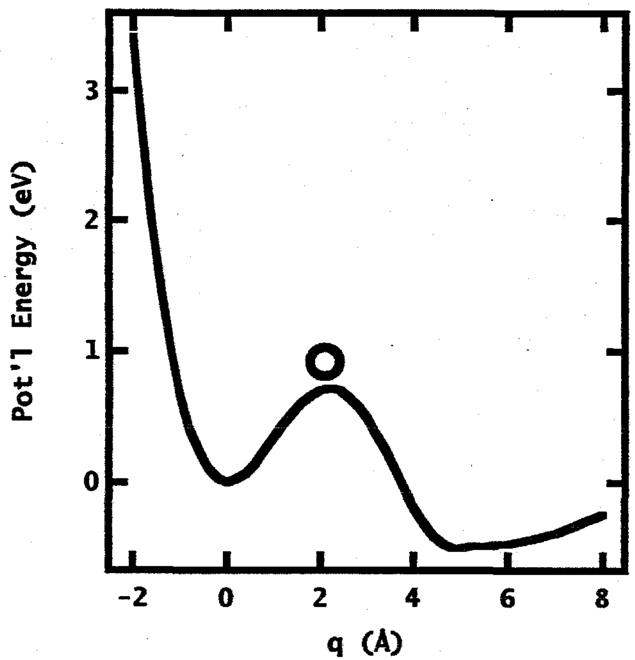


Stages

- Mechanical loading followed by thermalization
- Coordinate frame: Sitting on unreacted atom watching what is coming at you
- Capture athermal, mechanically loaded feature
  - $1/k = 1/k_{mech} + 1/k_{therm}$
- cf. NEZND and starvation kinetics:
  - **Another way to capture dissipation is through friction**
  - **Another way to derive reaction rates is through equations of motion**

Kinetic Derivation of TST





- Brownian motion - generalized Langevin equation
  - $m\, q''(t) = -dV(q(t))/dq - \int d\tau\, q'(\tau)\, \gamma(t-\tau) + F(t)$
  - **$F(t)$ - random force**
  - **γ - time-dependent friction kernel**

- Transform to a Fokker-Planck equation
  - $\partial\rho/\partial t = dV/dq\, \partial\rho/\partial p - p\, \partial\rho/\partial q + \eta\, \partial/\partial p(p\rho + k_B T \partial\rho/\partial p)$
  - **η - friction constant**
  - **ρ - density of points at (q, p) in phase space**

- Assume
  - **Boltzmann velocity distribution**
  - **Parabolic barrier**
  - **Low friction**

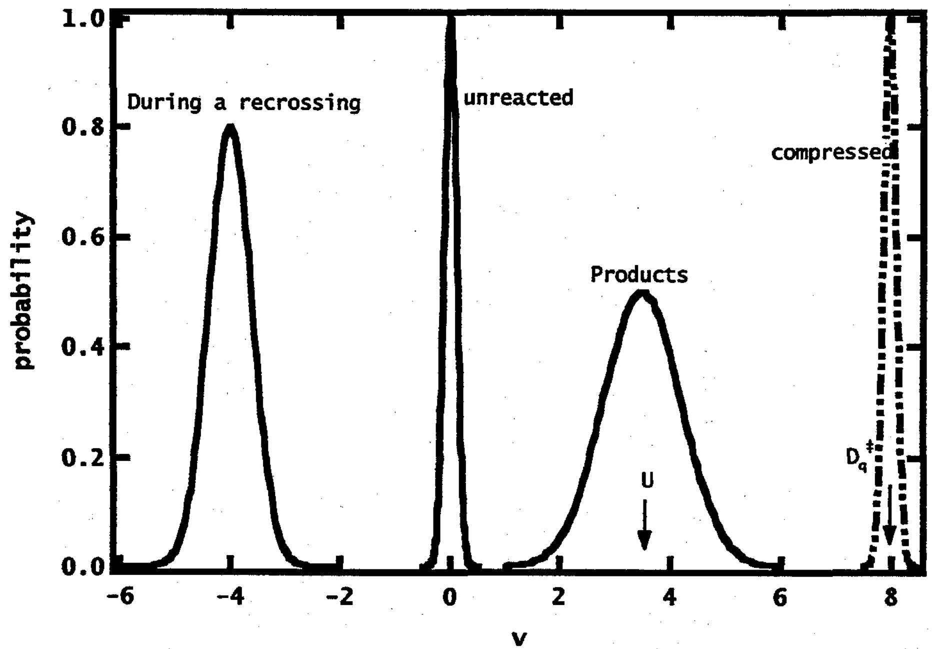
- $k_{TST} = \nu \exp(-E_a/k_B T)$ - Kramers (1940)

Kinetic Derivation of TST with Shock

Solve Fokker-Planck equation with shock ICs

- **Project D on reaction coordinate: D_q**
- **Boltzmann velocity distribution centered at D_q**
- **Straight-line loading to TS: $D_q^{\ddagger}$, $E_{a,D}$**

- Ignore
  - **Temperature changes**
  - **Evolution of D to U**
  - **Recrossings, couplings, memory, multi-step rxns**



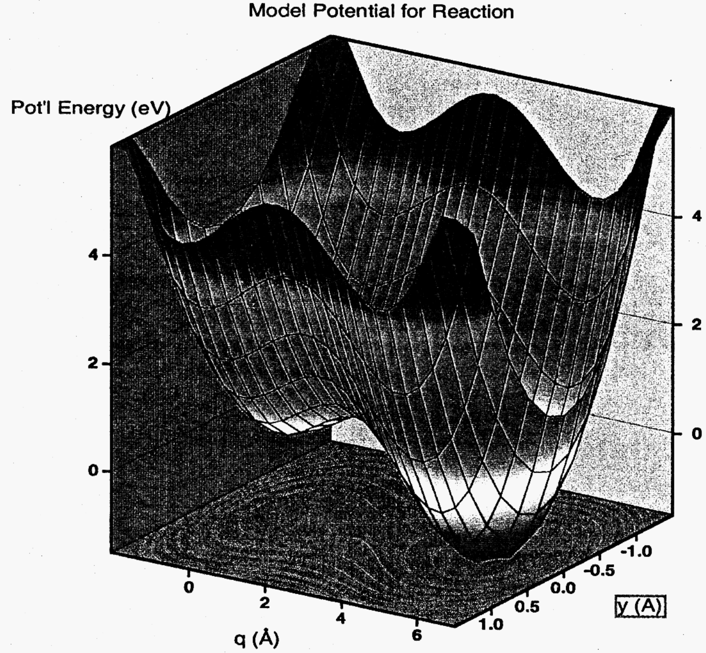
Shock-Dependent, Anisotropic Kinetics

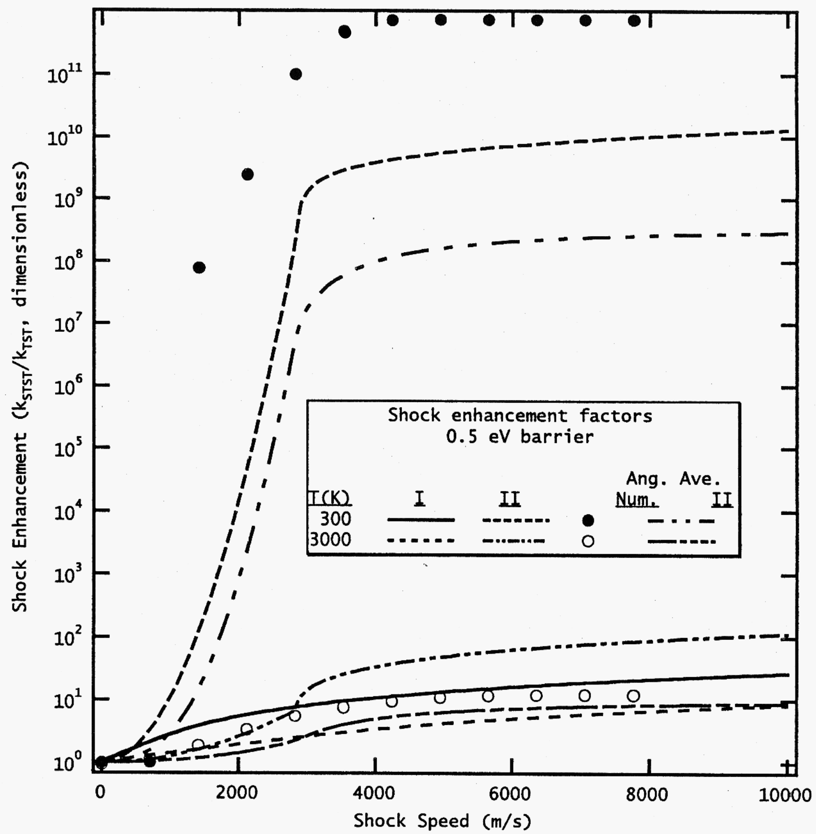
- $1/2\ m\ D_q^2 < E_a$
  - $k_{STST} = \nu \exp(-(E_a - 1/2\ m\ D_q^2)/k_B T)$
  - Reduce barrier by kinetics energy

- $1/2\ m\ D_q^2 > E_a$
  - $k_{STST} = \nu\ (\exp(-1/2\ m\ D_q^{\ddagger 2})/k_B T) + D_q^{\ddagger} / v_{therm}\ \mathrm{erfc}(1/2\ m\ D_q^{\ddagger 2}))$
  - $D_q^{\ddagger} = \sqrt{(D_q^{\ddagger 2} - 2\ E_a/m)}$
  - Combination of thermal and convective contributions

Numerical Comparison

- **Solve Langevin equation numerically**
  - Frictionless, no recrossing, 1D
  - Velocity Verlet algorithm
  - All trajectories start in the reactant well





07 August, 2001

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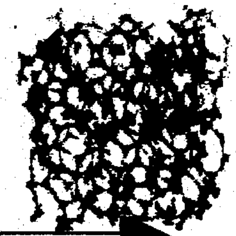
Future Extensions

- Velocity distribution - S. Chandrasekhar (1954)
  - $v(t) = v - U - (D - U) \exp(-\langle\gamma\rangle t)$
- Temperature dependence - Pollack, Talkner, and Berezhkovski (1997)
  - $T(t) = T_f + (T_0 - T_f) \exp(-\langle\gamma\rangle t)$
- Re-derive Kramers - Grote & Hynes (1980)
- Confinement - imitate porosity, defects, etc. with confinement parameter
- Do real shock simulation



Summary

Simple Extension of TST

- Anisotropy
- Shock-strength dependence
- Saturation
- Extendible to frictional cases, multidimensional, multiple rxn steps
- Couple kinetics and constitutive models
- Model constitutive properties when TST applicable
- Rate-limiting step may change with shock strength