



UNIVERSITY OF NEBRASKA-LINCOLN

Physics & Astronomy

# Chemical reaction rate and transition of $\text{Fe}_x\text{O}_y$

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# Reaction rate

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The change in the concentration of a reactant or a product with time (M/s).

Reactant  $\rightarrow$  Products

A  $\rightarrow$  B

change in number of moles of B

Average rate =  $\frac{\text{change in number of moles of B}}{\text{change in time}}$

$$= \frac{\Delta(\text{moles of B})}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

Since **reactants** go away with time: Rate =  $-\frac{\Delta[A]}{\Delta t}$



# Rate Law & Reaction Order

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- The reaction *rate law expression* relates the rate of a reaction to the concentrations of the reactants.
- Each concentration is expressed with an order (exponent).
- The rate constant converts the concentration expression into the correct units of rate ( $\text{Ms}^{-1}$ ).

For the general reaction:  $aA + bB \rightarrow cC + dD$

$$\text{Rate} = k [A]^x [B]^y$$

**k: reaction constant**

## Reaction Order

$x$  and  $y$  are the reactant orders determined from experiment.

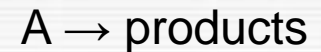
$x$  and  $y$  are **NOT** the stoichiometric coefficients.



# Time dependence of concentration

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For a first order process, the rate law can be written:



$$\text{Rate (M/sec)} = -\frac{\Delta[A]}{\Delta t} = k[A] \quad \text{average rate}$$

$$\text{Rate (M/sec)} = -\frac{d[A]}{dt} = k[A] \quad \text{instantaneous rate}$$

Integrate it:  $\ln\left(\frac{[A]}{[A_0]}\right) = -kt$        $k$ : reaction constant

$$\frac{[A]}{[A_0]} = e^{-kt} \quad \text{or} \quad [A] = [A_0]e^{-kt}$$

The concentration of a reactant governed by first order kinetics falls off from an initial concentration **exponentially with time**.



## Activation Energy and Arrhenius equation

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The dependence of the **rate constant  $k$  of a chemical reaction** on the absolute **temperature  $T$**  (in kelvins), where  $A$  is the pre-exponential factor (or simply the prefactor),  $E_a$  is the activation energy, and  $R$  is the universal gas constant

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

The only difference is the energy units of  $E_a$

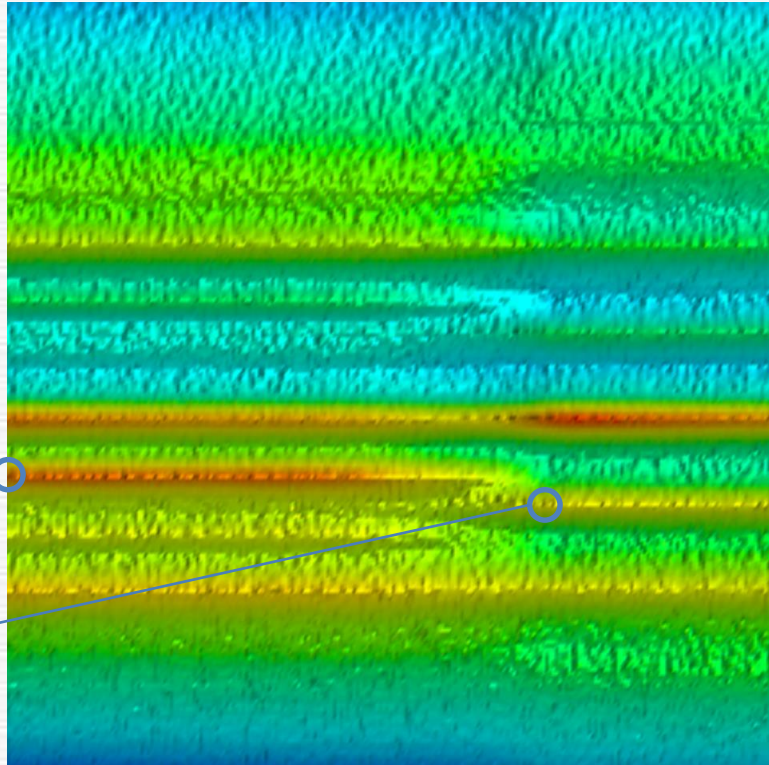
$$\ln\left(\frac{[A]}{[A_0]}\right) = -kt \quad \text{Then } \ln\left(\frac{[A]}{[A_0]}\right)/(-t) = A^* \exp(-E_a/RT)$$

$$\frac{1}{t} = A' e^{-\frac{E_a}{RT}}$$

$$\ln\left(\frac{1}{t}\right) = \ln(A') - \frac{E_a}{R} \left(\frac{1}{T}\right)$$



# RHEED intensity and Exponential decay



alpha-Fe<sub>2</sub>O<sub>3</sub> → Fe<sub>3</sub>O<sub>4</sub>

alpha-Fe<sub>2</sub>O<sub>3</sub>

Fe<sub>3</sub>O<sub>4</sub>

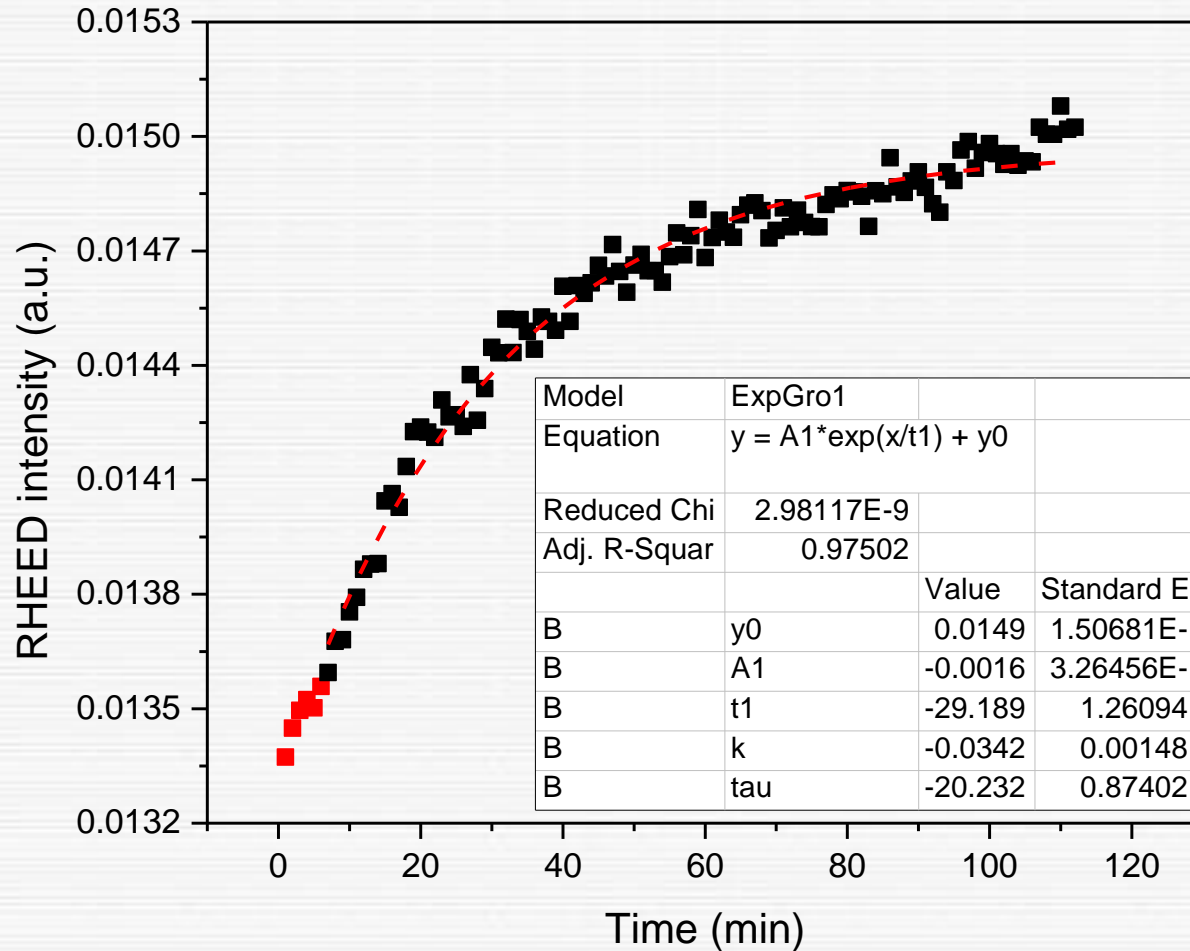
Exponential decay

$$N(t) = N_0 e^{-t/\tau}$$

$\tau$ : mean lifetime (or simply the lifetime or the exponential time constant)

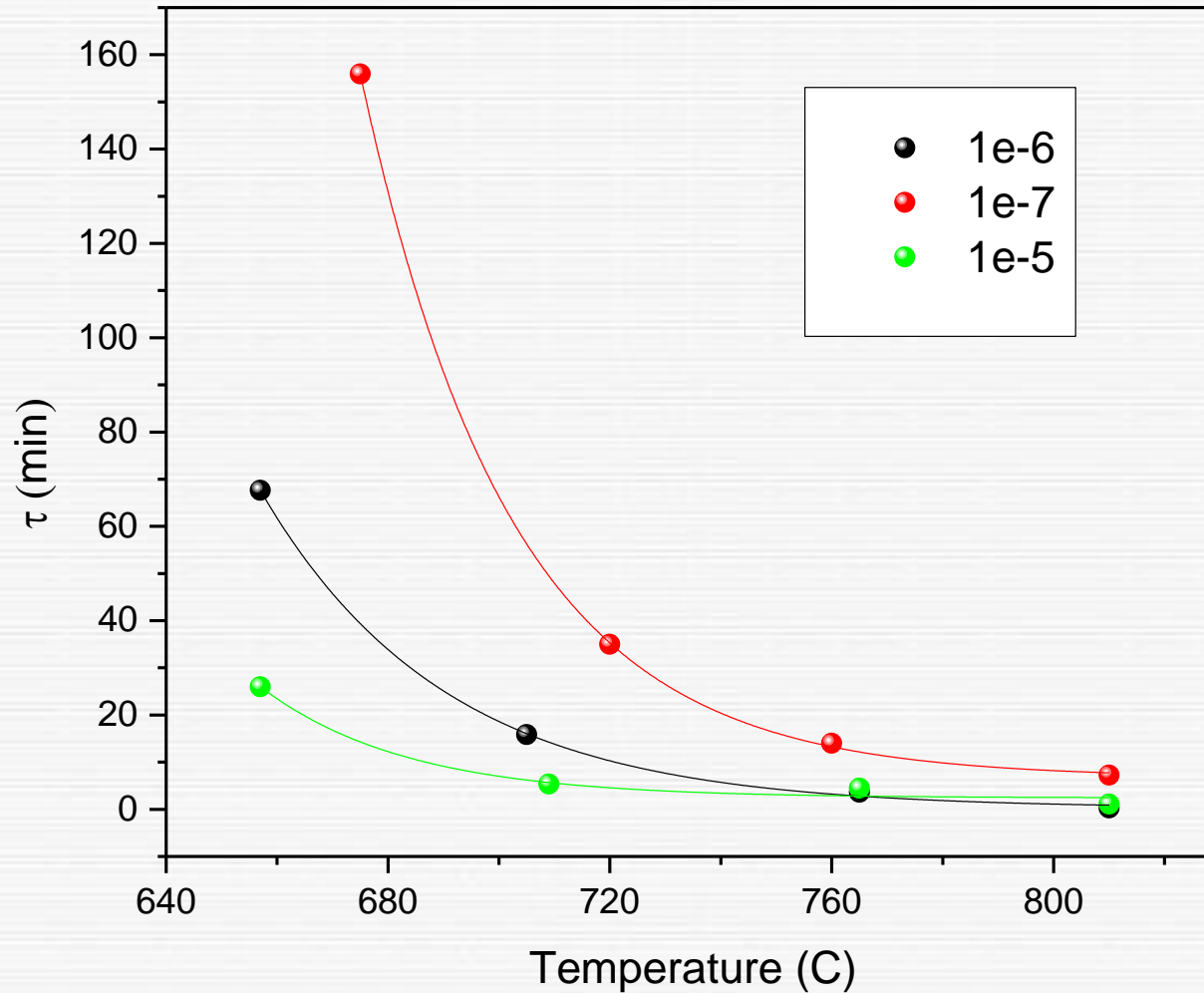


# Exponential fitting of RHEED intensity evolution





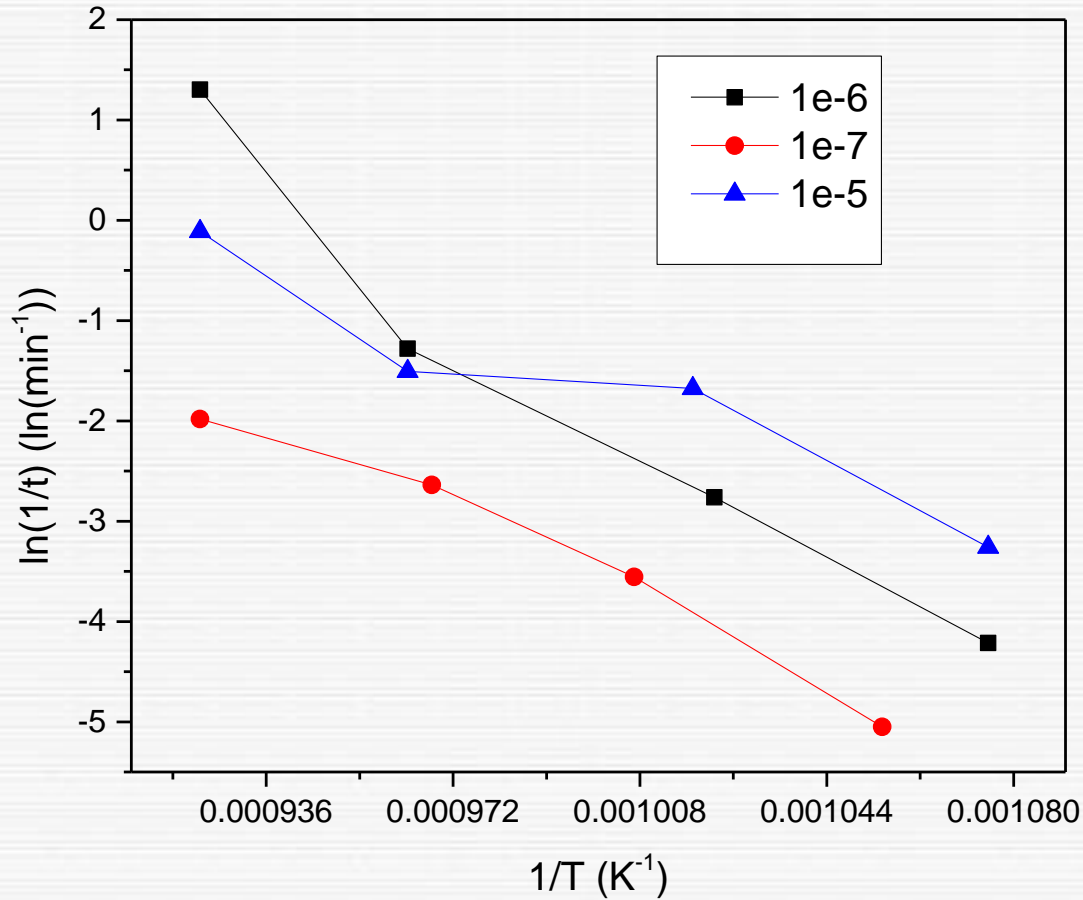
# Reaction lifetime with temperature







# Activation Energy



$$\ln\left(\frac{1}{t}\right) = \ln(A') - \frac{E_a}{R} \left(\frac{1}{T}\right)$$



**Thank you for your time!**