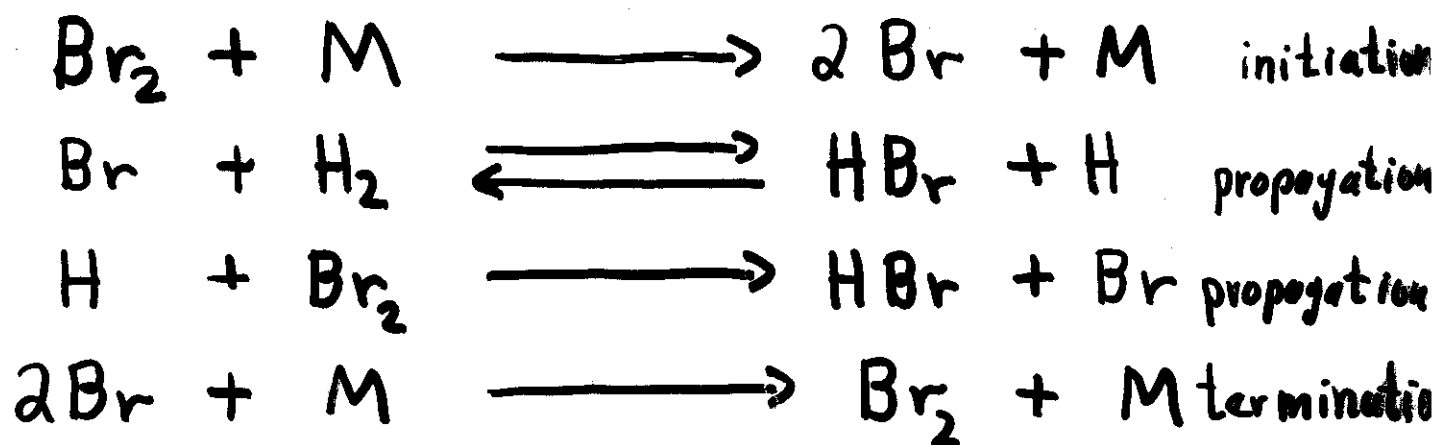
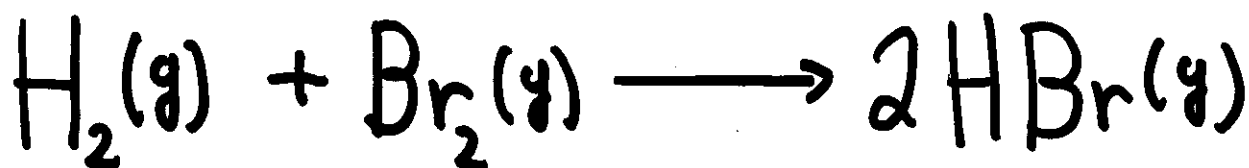
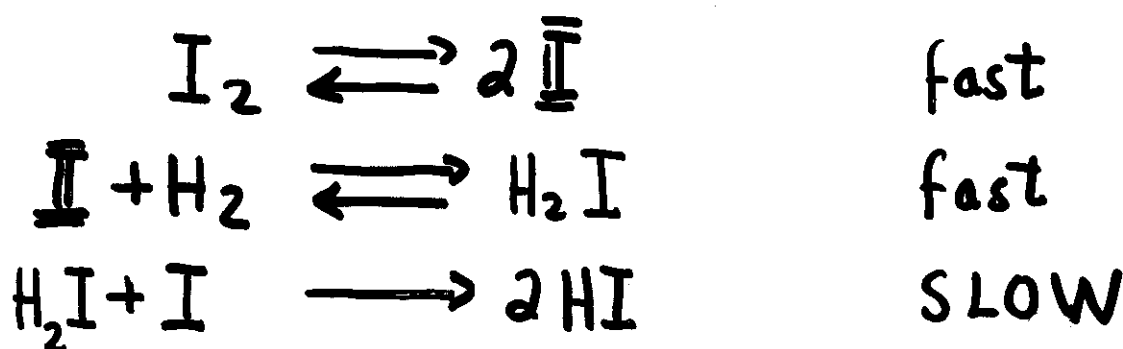
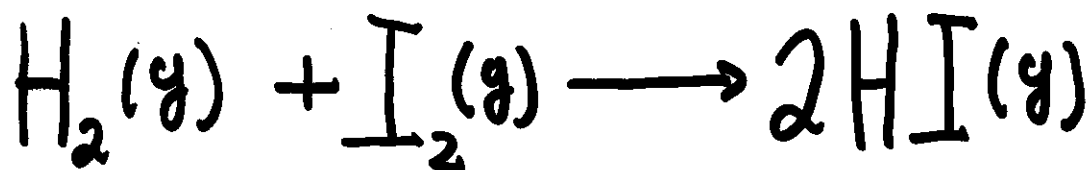


LECTURE 32/36

NOV-27-02

- MECHANISMS

Mechanisms



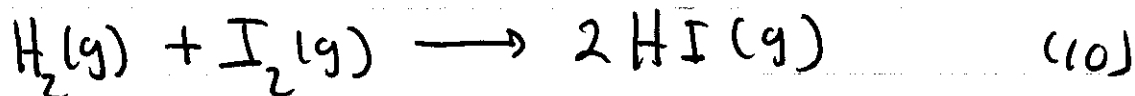
GIVEN BY:

$$r = k_1 [\text{NO}_2]^2 \quad (8)$$

AND

$$k_3 = k_1 \quad (9)$$

THE SIMPLE REACTION

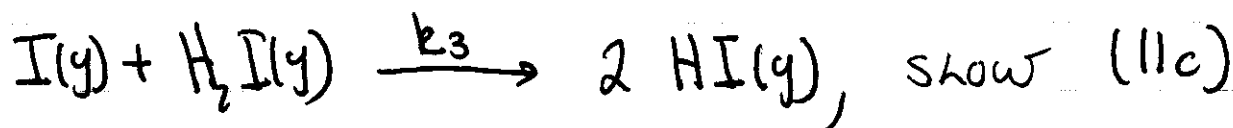
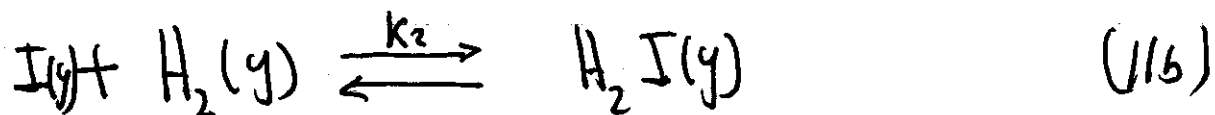
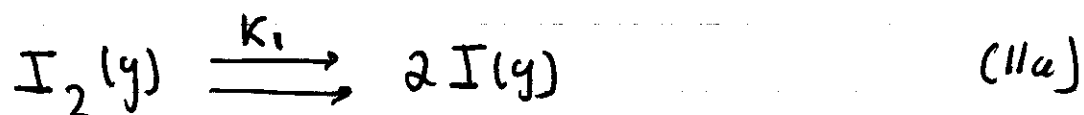


UNTIL RECENTLY, AS
WAS CONSIDERED, AN ELEMENTARY

REACTION. PRESENTLY WE KNOW THAT

REACTION DEPICTED BY EQ. (10) FOLLOWS

A THREE STEP MECHANISM



WHERE THE THIRD STEP, EQ. (11c), IS
VERY SLOW COMPARED WITH ^{THE FIRST TWO} STEPS.

THUS STEP THREE CONTROLS THE RATE, AND

WE CAN WRITE THE RATE AS

$$r = k_3 [I] [H_2I]. \quad (12)$$

BUT EQ (12) EXPRESSES THE RATE AS A

FUNCTION OF INTERMEDIATES, WHICH

CANNOT BE MEASURED. REMEMBER THAT

THE EXPERIMENTAL RATE LAW RELATES

THE MEASURED RATE OF THE REACTION

WITH THE CONCENTRATIONS OF

REACTANTS AND PRODUCTS BUT NOT

THE INTERMEDIATES.

SO, WE HAVE TO RE EXPRESS EQ. (12) IN
THE CONCENTRATIONS OF
TERMS OF REACTANTS AND PRODUCTS.

TO DO SO, WE FIRST RECOGNIZE THAT FIRST
TWO STEPS REACH EQUILIBRIUM BECAUSE
THEY ARE MUCH FASTER THAN THE THIRD
STEP,

$$K_1 = \frac{[I]^2}{[I_2]} \quad (13a)$$

$$K_2 = \frac{[H_2I]}{[I][H_2]} \quad (13b)$$

FROM EQ (13) WE FIND THE FOLLOWING
RELATION

$$K_1 K_2 = \frac{[I][H_2I]}{[I_2][H_2]} \quad (14)$$

THUS, EQ. (12) REDUCES TO

$$r = k_3 K_1 K_2 [H_2][I_2] \quad (15)$$

EQUATION (15) IS CONSISTENT WITH THE
EXPERIMENTAL RATE LAW

$$r = k^{\text{exp}} [H_2][I_2],$$

WITH THE FOLLOWING EXPRESSION FOR
THE EXPERIMENTAL RATE CONSTANT

$$k^{\text{exp}} = k_3 K_1 K_2, \quad (16)$$

WHICH IS A PREDICTION ASSOCIATED TO
PROPOSED
THE MECHANISM, I.E. EQ(11).

IT IS NOT RARE THAT TWO OR MORE MECHANISMS
COULD BE CONSISTENT WITH THE EXPERIMENTAL
RATE LAW. IN THIS CASE, ONE
MECHANISM CAN BE OVERRULED

IF THE INTERMEDIATE SPECIES ASSOCIATED TO A MECHANISM ^{CAN NOT} BE IDENTIFIED. NOTICE THAT INTERMEDIATES ARE SHORT LIVED COMPARED WITH REACTANTS AND PRODUCTS.

IN OTHER WORD, THE CHARACTERISTIC TIME ASSOCIATED TO THE OVERALL REACTION

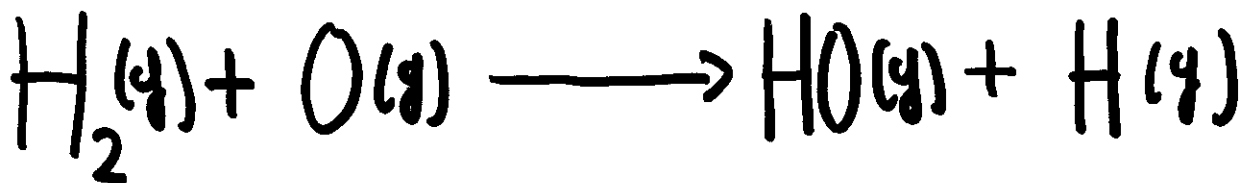
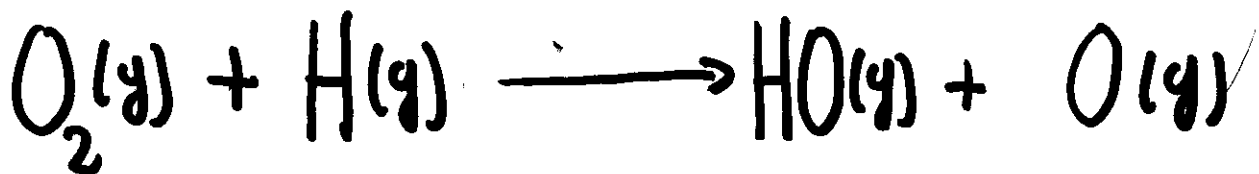
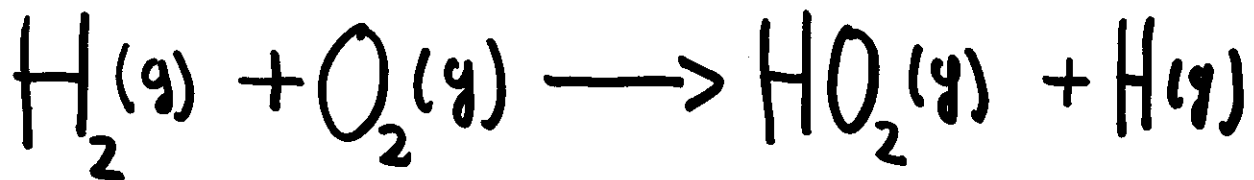
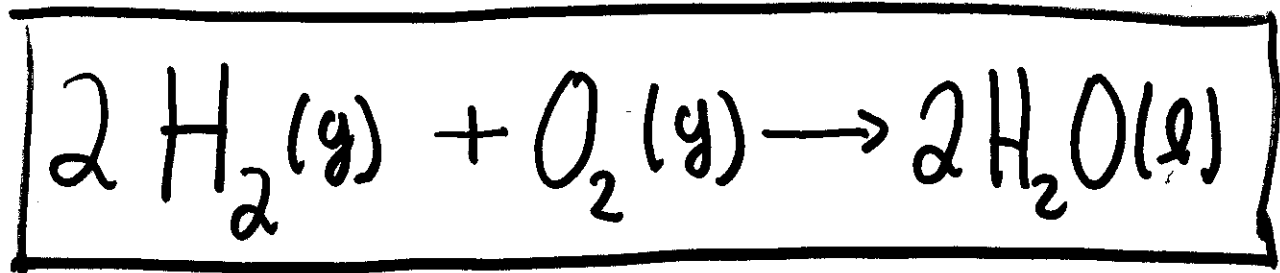
^{MUCH} IS GREATER THAN THE CHARACTERISTIC TIMES ASSOCIATED (TO) THE REACTIONS INVOLVING THE INTERMEDIATES.

CONSEQUENTLY, WITHOUT MORE INFORMATION

AT SHORTER TIME SCALES THAN THE

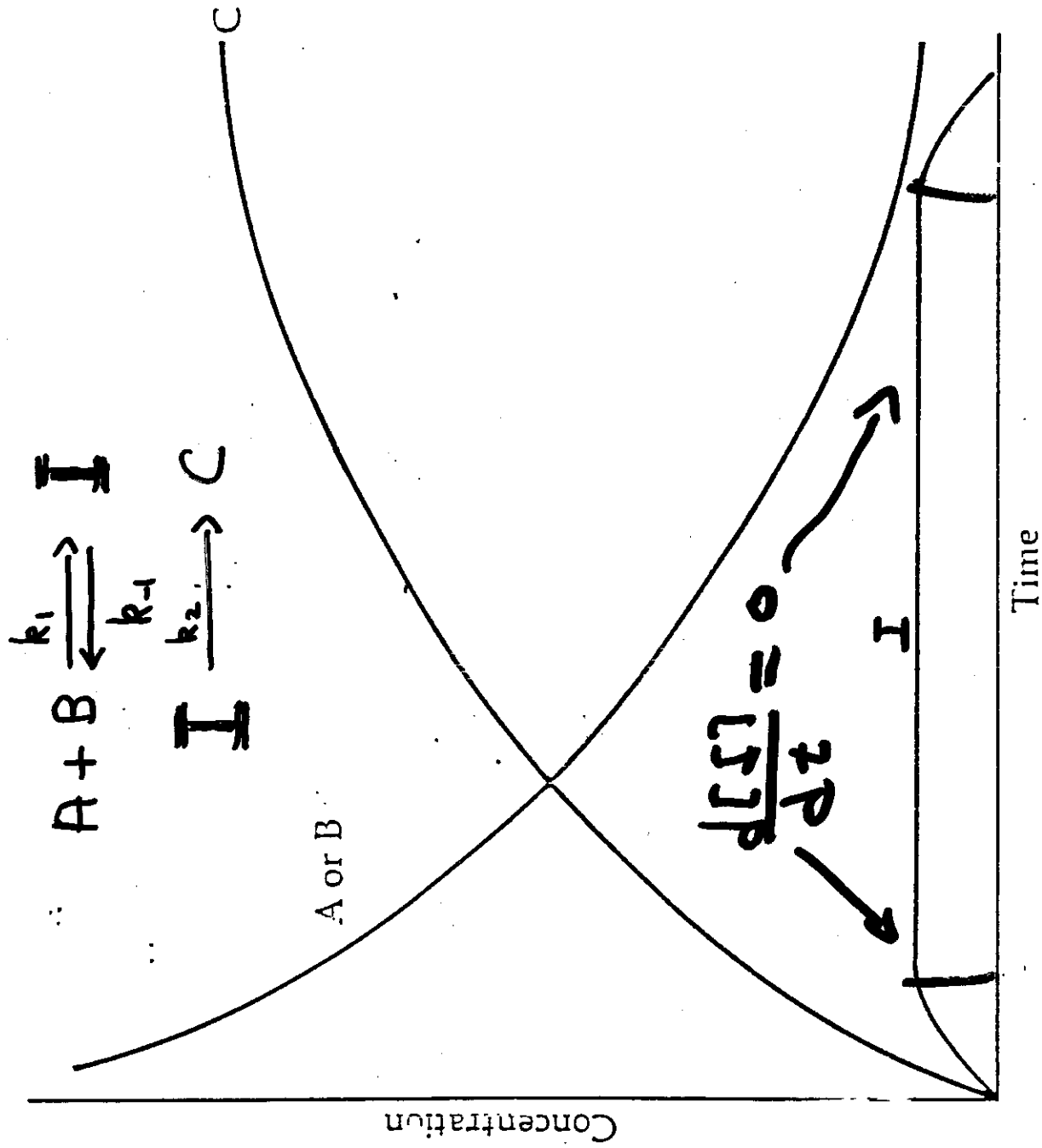
OVERALL REACTION'S CHARACTERISTIC TIME,

WE CANNOT RULED OUT MECHANISMS THAT ARE CONSISTENT WITH THE EXP. RATE LAW.



At 298°K $\Delta G_{\text{rxn}}^\circ = -474.48 \text{ kJ} < 0$

dependence of concentrations of species involved in the reaction $A + B \rightarrow C$. Note that the concentration of the intermediate I increases to a certain small value, remains constant during most of the reaction, and then decreases to zero. The constancy of $[I]$ is the basis of the steady-state approximation.



STEADY STATE APPROXIMATION

IN A MULTIPLE STEP MECHANISM, WE USUALLY FIND ONE OR MORE INTERMEDIATE SPECIES THAT DO NOT APPEAR IN THE OVERALL REACTION. IN OTHER WORDS, THE INTERMEDIATES DO NOT ACCUMULATE UP TO DETECTABLE CONCENTRATIONS, AND THESE SPECIES ARE VERY REACTIVE COMPARED WITH THE REACTANTS AND PRODUCTS,

$$[I] \ll [R] \quad (a)$$

$$[I] \ll [P]. \quad (b)$$

ALSO WE FREQUENTLY ENCOUNTER

MECHANISMS WITH REVERSIBLE STEPS

IN WHICH AT LEAST ONE INTERMEDIATE

IS FORMED. FOR EXAMPLE WE CONSIDER
THE FOLLOWING TWO STEP MECHANISM



WHERE I IS AN INTERMEDIATE AND

$$K_1 = \frac{k_1^+}{k_1^-}. \quad (2c)$$

FROM EQ. (2) THE RATE OF CHANGE OF I IS GIVEN BY THE FOLLOWING EQUATION:

$$\frac{d[I]}{dt} = k_1^+[A][B] - k_1^-[I] - k_2[I]. \quad (3)$$

IN MANY CASES, THE INTERMEDIATES,

EXCLUDING AN INDUCTION TIME (INITIAL TIME),

REACH A STEADY STATE VALUE. IN OTHER

WORDS

$$\frac{d[I]}{dt} \approx 0. \quad (4)$$

NOTICE THAT THE INDUCTION TIMES HAVE TO BE QUITE SHORTER THAN THE OVERALL REACTION'S CHARACTERISTIC TIME.

USING EQS. (3) AND (4), WE FIND THAT STEADY VALUE OF I IS GIVEN BY

$$[I]_{ss} = \frac{k_1^+ [A][B]}{k_1^- + k_2}. \quad (5)$$

THUS EQS (2) AND (5) YIELD

THE FOLLOWING RATE LAW

$$r = \frac{d[C]}{dt} = k_2 [I] \approx k_2 [I]_{ss} = \frac{k_2 k_1^+}{k_1^- + k_2} [A][B] \quad (6)$$

THERE FOR, EQ (2) PREDICTS A

SECOND ORDER RATE LAW WITH RATE CONSTANT

$$k = \frac{k_2 k_1^+}{k_{-1}^- + k_2}, \quad (7)$$

WHICH CAN BE COMPARED WITH THE
EXPERIMENTAL RATE CONSTANT, IF WE
KNOW THE VALUES OF k_1^+ , k_{-1}^- AND k_2 .

THE STEADY-STATE APPROXIMATION ASSUMES THAT
THE CONDITIONS EXPRESSED BY EQ. (1) AND
(4), ARE SATISFIED BY THE
CONSEQUENTLY
CHEMICAL SYSTEM, WE CAN SET THE
RATES OF CHANGE OF THE INTERMEDIATES
EQUAL TO ZERO AND SOLVE THE
ALGEBRAIC EQUATION FOR ALL THE
INTERMEDIATES.

FINALLY WE CAN EXPRESS THE RATE LAW

ASSOCIATED ^{TO} (WITH) THE MECHANISM

IN TERMS OF REACTANT AND PRODUCT

CONCENTRATIONS.

STEADY-STATE APPROXIMATION

- a) IDENTIFY THE INTERMEDIATES
- b) WRITE DOWN THE RATE OF CHANGE OF THE INTERMEDIATES ASSOCIATED TO THE MECHANISM.
- c) SET THE RATE EQ. EQUAL TO ZERO.
(S.S. APPROX).
- d) SOLVE FOR $[I]_{ss}$
- e) CALCULATE THE RATE LAW PREDICTED BY THE MECHANISM USING EITHER

$$r = - \frac{1}{\nu_R} \frac{d[R]}{dt} = \frac{1}{\nu_P} \frac{d[P]}{dt}$$