Heterogeneous Bunsen Reaction

Analysis & Experimental study of Chemical absorption of Sulfur dioxide and dissolution of Iodine into aqueous reacting system

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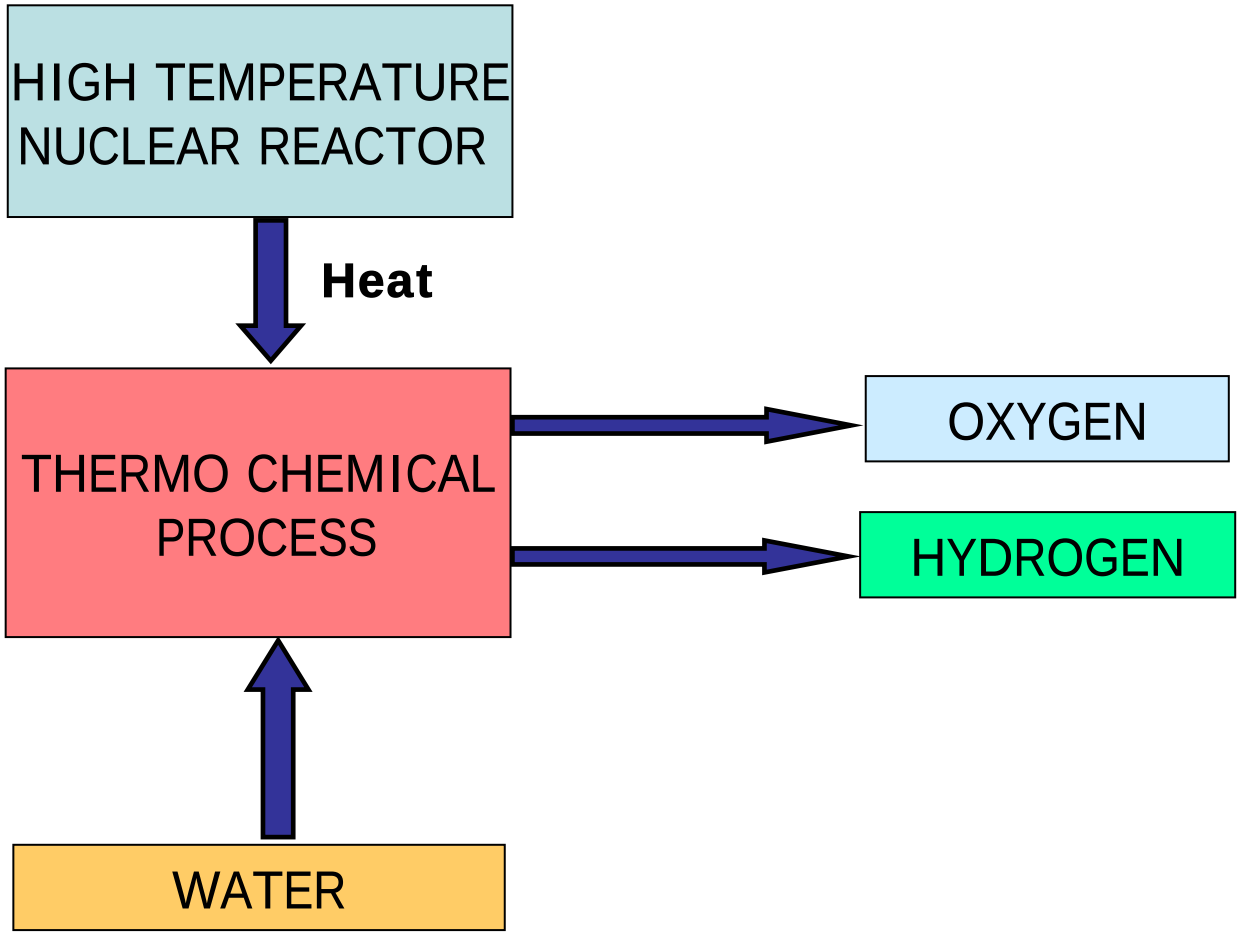
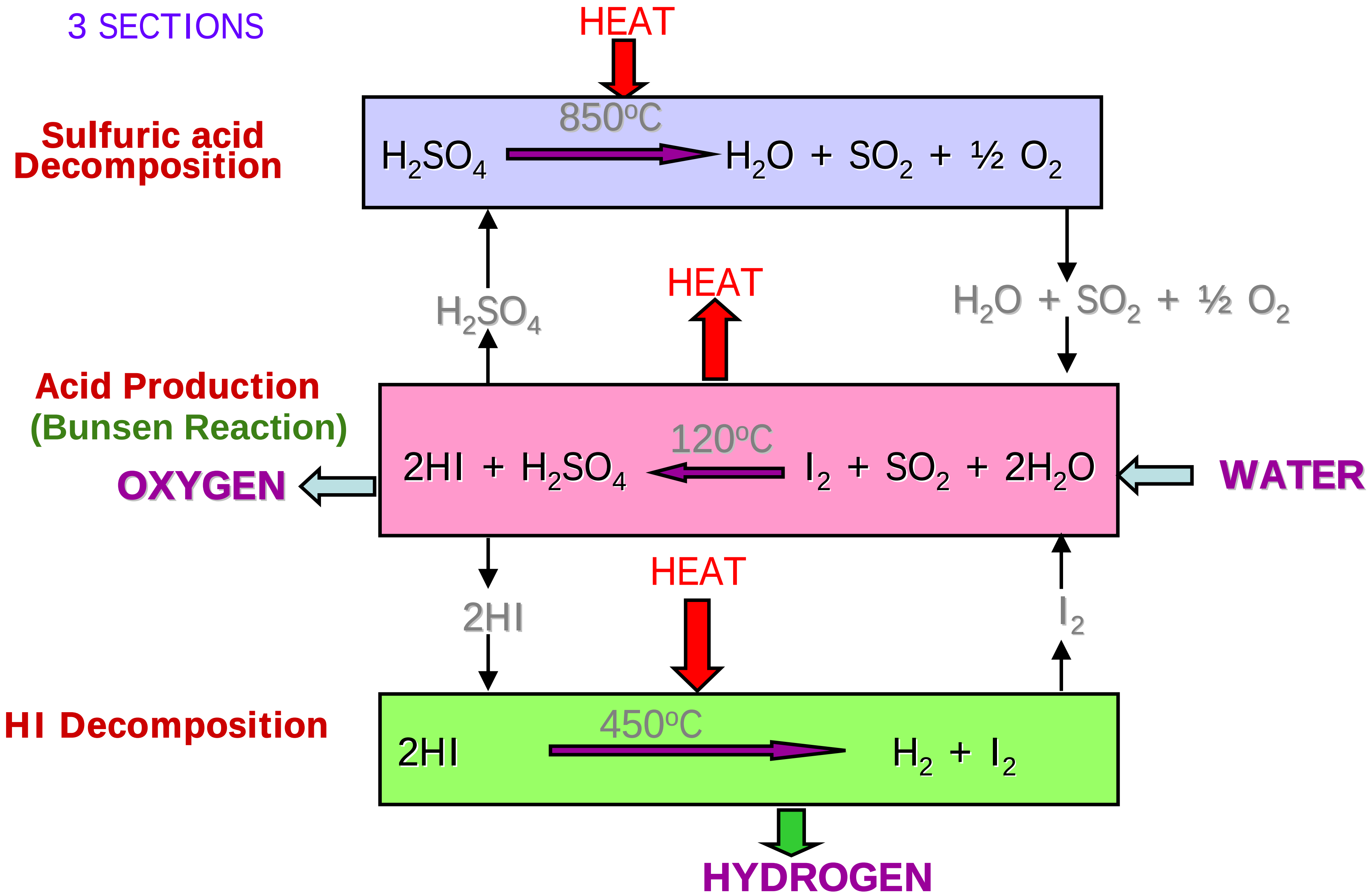
Thermo Chemical Process for H_2 Production



Iodine-Sulfur (I-S) Process – Reaction Scheme

3 SECTIONS



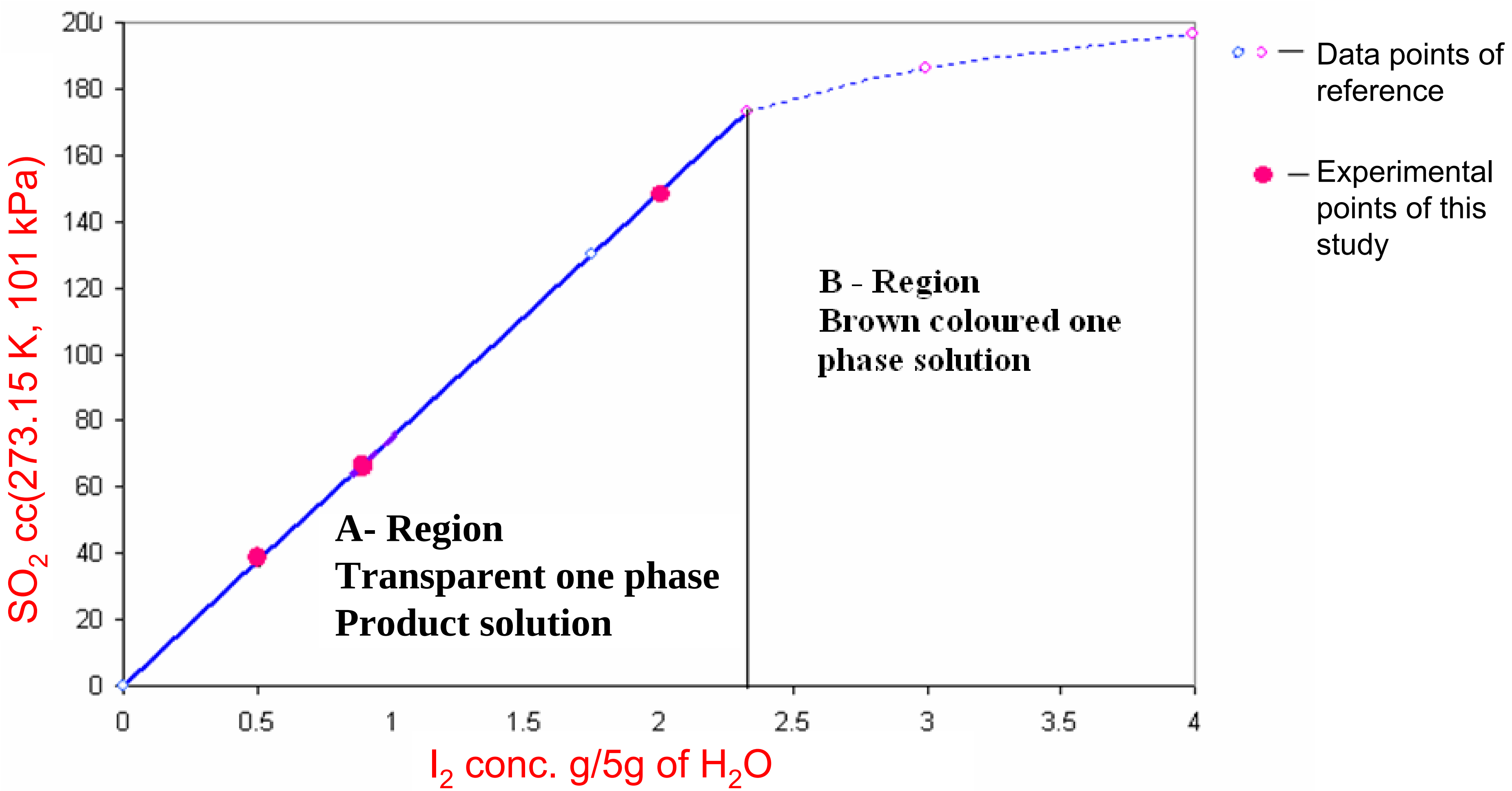
Heterogeneous Bunsen Reaction is the focus of this study

Objective is to derive crucial engineering information

A. Overall reaction rate
B. Reaction regimes
C. Controlling kinetic/mass transfer resistances
D. Coefficients
E. Enhancement factor

This information helps in chemical reactor selection, flow/contacting scheme choice and design

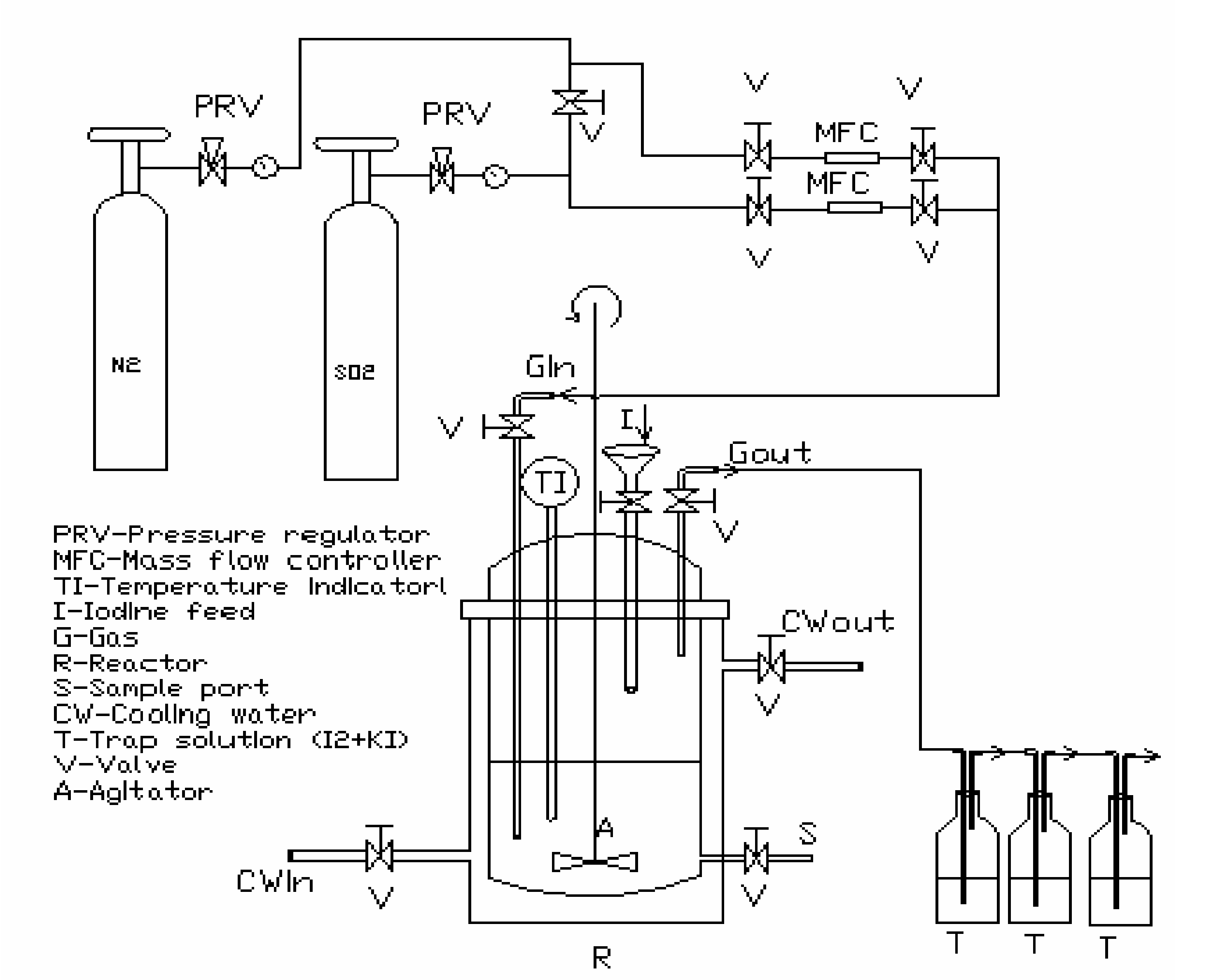
Region of experimental study



Absorption limit of SO_2 by the Bunsen reaction vs. the initial iodine fraction in the absorbent

Ref: KAORU ONUKI, et at., IS Process For thermo chemical Hydrogen Production JAERI - Review 94 – 006

Sketch of experimental setup



Bunsen reaction

stoichiometric : $SO_2 + I_2 + 2H_2O \longrightarrow 2HI + H_2SO_4$

with excess of I_2 & H_2O : $SO_2 + xI_2 + y\,H_2O \longrightarrow 2HI + H_2SO_4 + (x-1)\,I_2 + (y-2)\,H_2O$

is represented as follows for analysis

SO_2 , A + I_2 , B + H_2O ,Aq $\longrightarrow$ (H_2SO_4 +HI),Products

A(g) $\longrightarrow$ A(aq)

B(s) $\longrightarrow$ B(aq)

A(aq) + zB (aq) $\longrightarrow$ Products

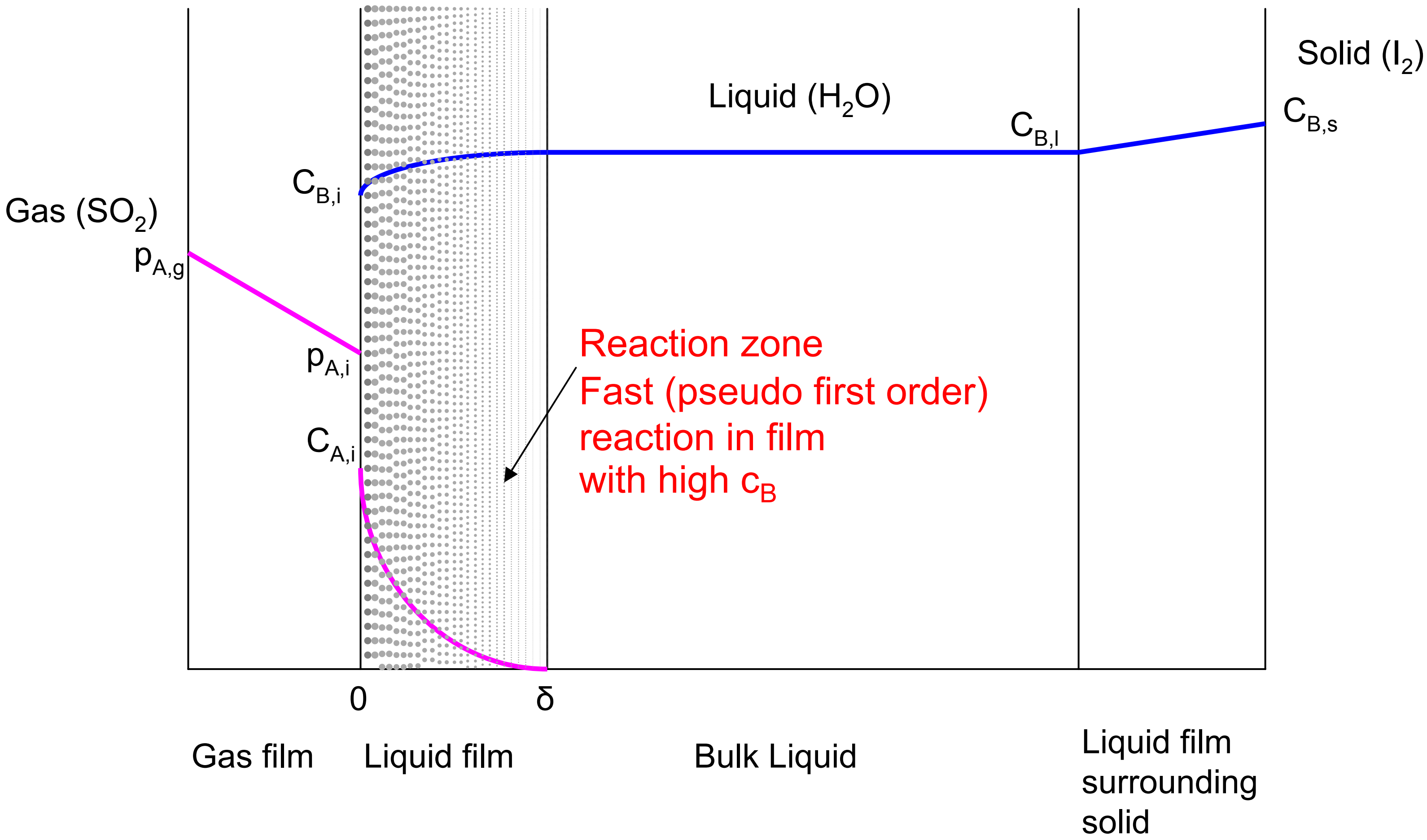
This multiphase process involving mass transfer and chemical reaction has following steps

1) Diffusion of SO_2 (species A) through gas film

2) Dissolution of Iodine (species B)

3) Diffusion and simultaneous chemical reaction in the liquid film

Concentration profiles based on film theory for gas (sulphur dioxide) – liquid (water) – solid (Iodine) system



Gas phase mass transfer rate is given by,

$$-r_A = k_g a(p_{Ag} - p_{Ai})$$

Rate of iodine dissolution is given by,

$$-r_B = k_s a_p (c_{Bs} - c_{Bl})$$

Liquid phase reaction rate is given by,

$$-r_A = k_1 c_A = \frac{-r_B}{z}$$

The overall rate of reaction is given by,

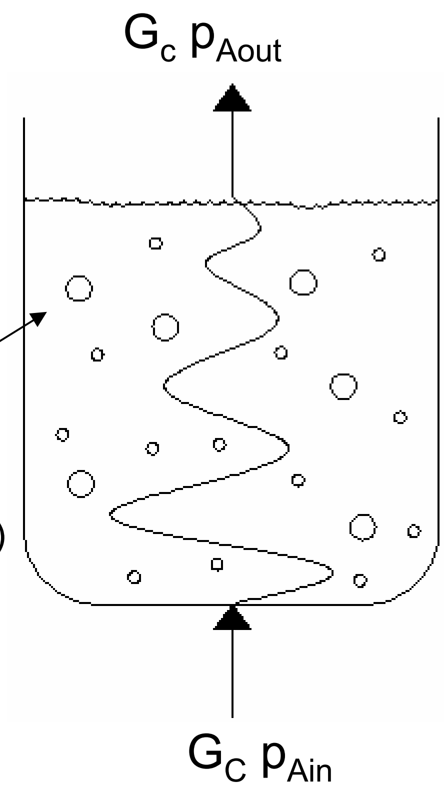
$$-r_A = \frac{p_{Ag}}{\left(\frac{1}{k_g a} + \frac{H}{k_l a E} + \frac{H}{k_1(1-\varepsilon)}\right)}$$

Gas film resistance | Liquid film resistance | kinetic resistance

Mass balances for the diffusing gas A and dissolving solid species B in the liquid film are as follows:

$$D_A \frac{d^2 c_A}{dx^2} = k_1 c_A \qquad D_B \frac{d^2 c_B}{dx^2} = z k_1 c_A$$

Reactor model schematic for analysis



V_r volume of G/L emulsion

$$= \frac{V_l \text{ (Batch of Reacting liquid)}}{(1-\varepsilon)}$$

At any instant c_B is same everywhere in the tank. However c_B decreases with time because of reaction with A (Yet much more than stoichiometric requirement during most of the batch time).

At the start $c_B = c_{Bo}$

At the end $c_B = c_{Bf}$

Mixed gas and completely mixed liquid.

E=Liquid film enhancement factor

$$= \frac{\text{Rate of uptake of A with chemical reaction}}{\text{Rate of uptake of A for straight mass transfer}}$$

Enhancement factor for infinitely fast reaction is,

$$E_i = 1 + \frac{D_B c_B H}{z D_A p_{Ai}}$$

Hatta no is,

$$H_a = \frac{\sqrt{k_1 D_A}}{k_l}$$

Henry's Law const is,

$$H = \frac{p_A}{c_A}$$

By overall mass balance across the reactor,

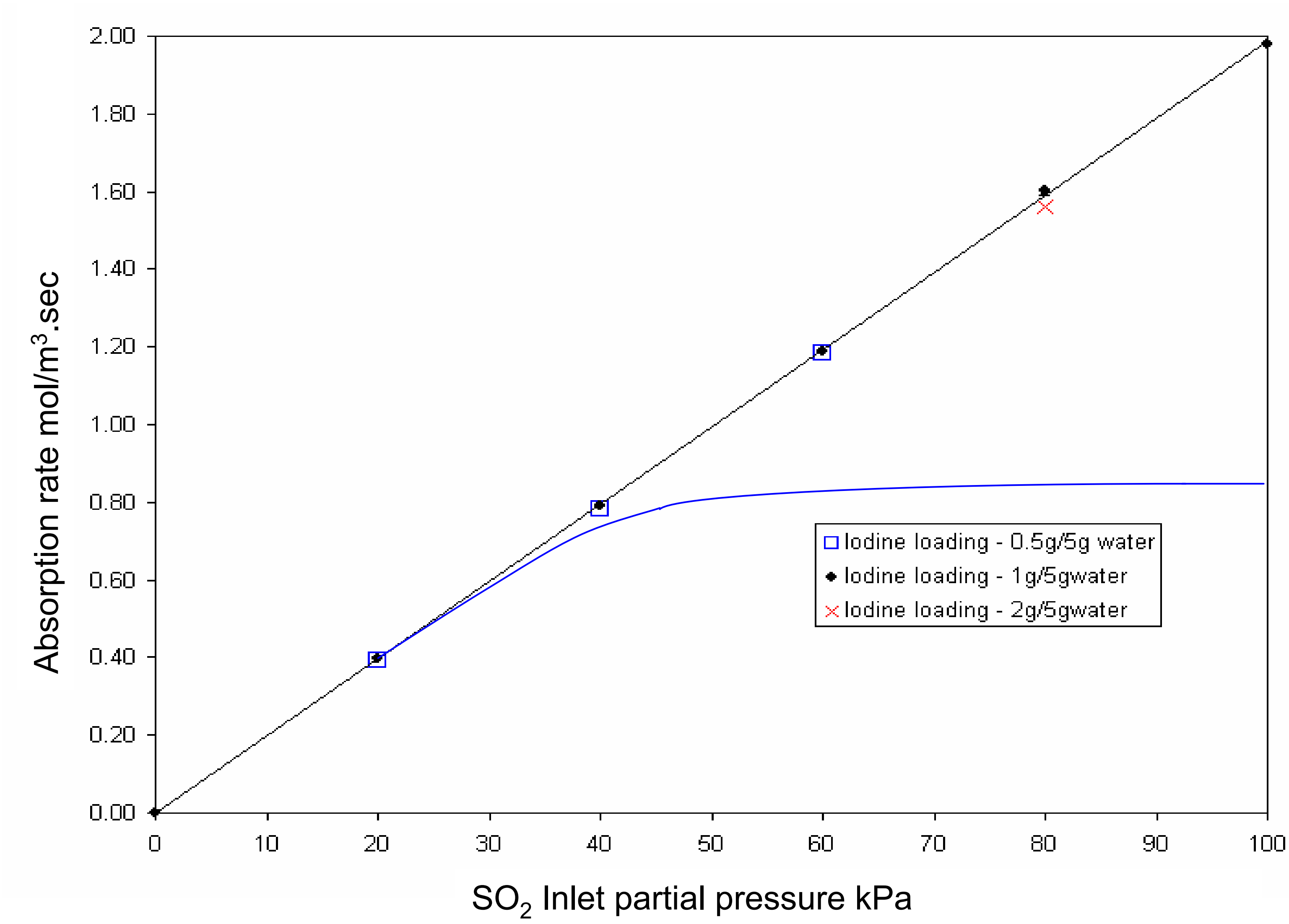
$$G_C \left[\frac{p_{Ain}}{P - p_{Ain}} - \frac{p_{Aout}}{P - p_{Aout}} \right] = (-r_A) V_r$$

Where, $V_r = \frac{V_l}{(1-\varepsilon)}$ and

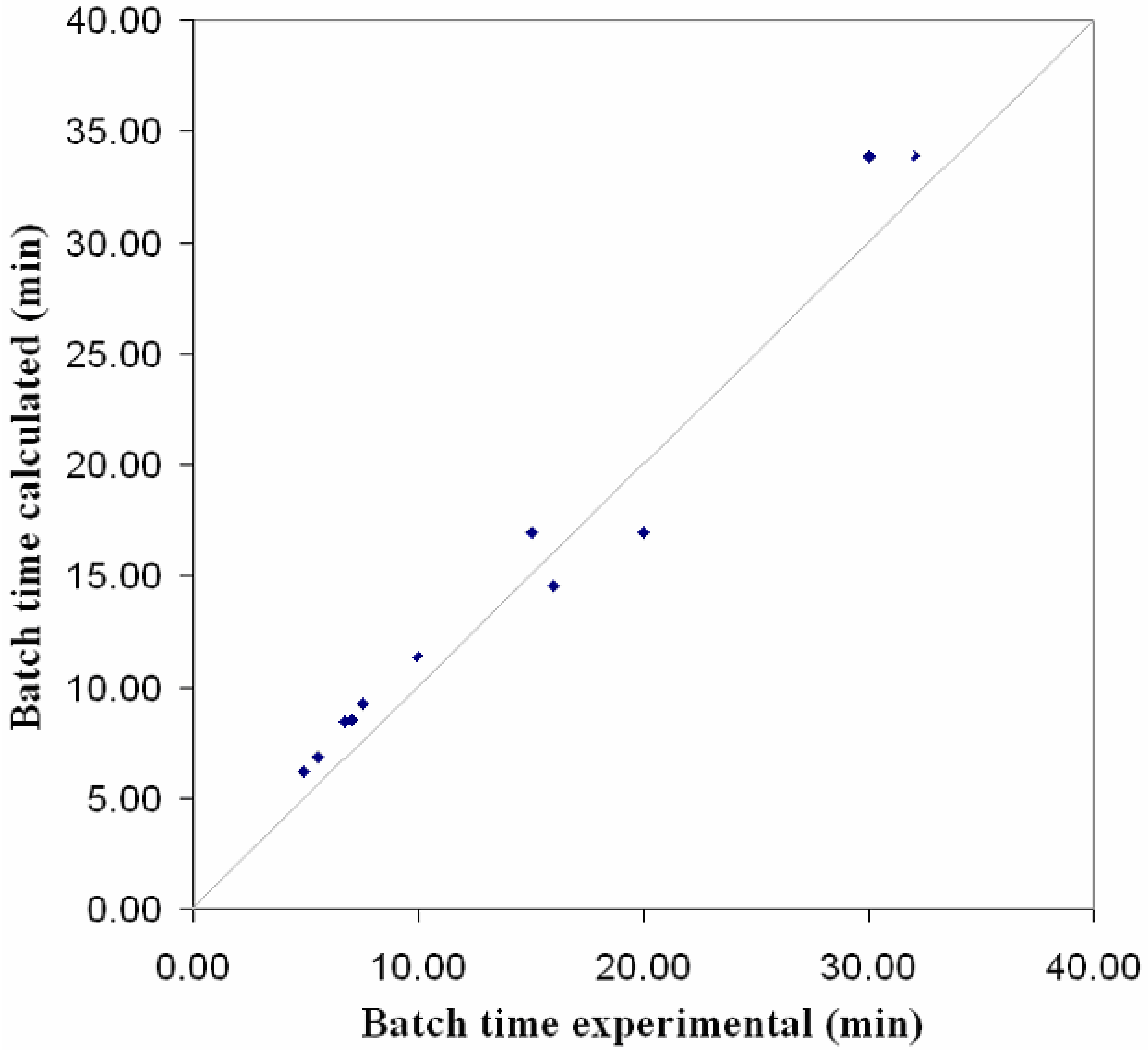
Batch time for the conversion of Iodine is calculated by,

$$t = \int_{c_{Bf}}^{c_{Bo}} \frac{(1-\varepsilon) dc_B}{-r_A z}$$

SO_2 absorption rate vs. SO_2 partial pressure for different Iodine loading



Batch time calculated vs. Batch time experimental



Typical parameters and values for Bunsen Reaction analysis

Batch time (calculated) (min)	t_{calc}	34
Batch time (experimental) (min)	t_{exp}	30
Gas film resistance (Pa m^3 s/kmol)	$1/(k_g a)$	$1.1x10^6$
Liquid film resistance (Pa m^3 s/kmol)	$H/(k_l aE)$	$1.0x10^7$
Liquid bulk resistance (Pa m^3 s/kmol)	$H/(k_1(1-\varepsilon))$	$7.5x10^2$
Hatta no	Ha	3.4
Enhancement factor (calculated)	E	2.1
Enhancement factor (experimental)	E	2.2
Solid dissolution parameter	$(k_s a_p D_A^2)/(4k_l D_B)$	$1.6x10^{-6}$

Conclusions

1) SO_2 absorption rate in chemically reacting system of Bunsen Reaction is experimentally studied and found to be a linear function of partial pressure (0-100 kpa) of SO_2 in inlet gas stream at atmospheric pressure. This functional relation is expected to hold good even under prototypical conditions of Bunsen Reaction
2) Multiphase Bunsen Reaction can be viewed as 'Fast pseudo first order' due to high concentration/rate of dissolution of Iodine and reaction zone is located in Liquid film near Gas-Liquid interface
3) Liquid film resistance constitutes ~90% of overall resistance
4) Experimental and theoretical results of this study indicated that this complex reacting system can be analyzed by invoking judicious simplifying assumptions for deriving practical engineering information
5) Rigorous model requires accurate thermodynamic, transport and physical properties
6) This study helps in selection/design of multiphase chemical reactor under prototypical conditions

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THANK YOU