INTRODUCTION LECTURE CBE 60544 TRANSPORT PHENOMENA January 15, 2014

TRANSPORT PHENOMENA

 "name is from the book from 1960 by Robert Bird, Warren Stewart and Ed Lightfoot.



ONE NOVELTY

TABLE I. SCHEMATIC DIAGRAM OF THE ORGANIZATION OF TRANSPORT PHENOMENA Entity Being Transported — Type of Transport -Mass Energy Momentum 16 DIFFUSIVITY DAR 8 THERMAL CONDUCTIVITY & Fourier's law of heat conduction Temperature, pressur-and composition dependence of & Kinetic theory of & TRANSPORT BY MOLECU-LAR MOTION 1 VISCOSITY # Fick's law of diffusion Newton's law of vis-cosity Temperature, pressure, and composition dependence of μ Kinetic theory of μ Temperature, pressure, and composition dependence of DAB Kinetic theory of DAB 17 SHELL MASS BALANCES Concentration profiles Average concentration Mass flux at surfaces 9 SHELL ENERGY BALANCES Temperature profiles Average temperature Energy flux at surfaces 2 SHELL MOMENTUM BALANCES Velocity profiles Average velocity Momentum flux at surfaces TRANSPORT IN LAMINAR FLOW OR IN SOLIDS, IN ONE DIMENSION 18 EQUATIONS OF CHANGE (MULTICOMPONENT) Equations of continuity for each species Equation of motion for forced and free convection 3 EQUATIONS OF CHANGE (ISOTHERMAL) Equation of continuity 10 EQUATIONS OF CHANGE (NONISOTHERMAL) Equation of continuity TRANSPORT IN AN ARBITRARY CONTINUUM Equation of motion for forced and free convection Equation of energy (nonisothermal) Equation of motion convection Equation of energy (multicomponent) Equation of energy (isothermal) (nonmochernal) 11 ENERGY TRANSPORT WITH TRANSPORT WITH TANSPORT WITH VARIABLES Unsteady head con-duction Heat conduction in viscous flow Two-dimensional heat conduction in solids Boundary-layer energy transport 19 MASS TRANSPORT WITH TWO INDEPENDENT VARIABLES Unsteady diffusion TRANSPORT IN LAMINAR FLOW OR IN SOLIDS, WITH TWO INDEPENDENT VARIABLES 4 MOMENTUM TRANSPORT WITH TWO INDEPENDENT VARIABLES Unsteady viscous flow Diffusion in viscous flow Two-dimensional viscous flow Ideal two-dimensional flow Boundary-layer mo-mentum transport Two-dimensional diffu-sion in solids Boundary-layer mass transport 20 TURBULENT MASS TRANSPORT Time-smoothing of equations of change Eddy diffusivity 12 TUBULENT ENERGY TANSPORT Time-smoothing of equations of change Eddy thermal con-ductivity Turbulent temperature profiles TRANSPORT IN TURBULENT 5 TURBULENT MOMENTUM TRANSPORT Time-smoothing of equations of change Eddy viscosity Turbulent concentration profiles Turbulent velocity profiles 13 INTERPHASE ENERGY TRANSPORT Heal-transfer coef-ficient à Dimensionless correla-tions (forced and free convection) 21 INTERPHASE MASS TRANSPORT Mass-transfer coefficient kg Dimensionless correla-tions (forced and free convection) 6 INTERPHASE MOMENTUM TRANSPORT Friction factor f TRANSPORT BETWEEN TWO PHASES Dimensionless correla-tions 14 RADIANT ENERGY TRANSPORT Planck's radiation law Stefan-Boltsmann law Geometrical problems Radiation through ab-sorbing media TRANSPORT BY RADIATION This book may be sind acther by "columns" or by "roms 22 MACROSCOPIC BALANCES (MULTICOMPONENT) Mass balances for each species Mochanical and total energy balance 15 MACROSCOPIC BALANCES (NONISOTHERMAL) Mass balance 7 MACROSCOPIC BALANCES (ISOTHERMAL) Mass balance TRANSPORT IN LARGE Momentum balance Mechanical and total energy balance Momentum balance Mechanical energy balance (Bernoulli equation)

EVOLUTION OF CHEMICAL ENGINEERING AS AN ACADEMIC DISCIPLINE



CHEMICAL ENGINEERING CORETODAY



HANS HAUG REACTOR SPECIALIST AT DUPONT



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RANDOM PAPER

Journal of Surgical Research 103, 55–60 (2002) doi:10.1006/jsre.2001.6340, available online at http://www.idealibrary.com on

Local Pharmaceutical Release from a New Hydrogel Implant

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Background. Solid hydrogel polymers can act as reservoirs for controlled drug release. The object of this study was to quantify release kinetics for a single example of a class of uniquely structured hydrogels. The polymer of this study belongs to a class of permanent implants that release pharmaceuticals by diffusion from an entangled cross-linked matrix rather than by absorption of the implant by the body. The crosslinked matrix (CLM) of this study is biocompatible and polymerized *in situ*, forming a solid that is mechanically bonded to the implant site. It can seal tissue as well as deliver drugs at predetermined rates. We evaluated dye and antibiotic egress and assessed release kinetics and retention of antibiotic activity following tent with a diffusion release mechanism. Antibiotic released from the tissue sealant was shown to be potent by consistent inhibition of *E. coli*.

Conclusion. Pharmaceutical release by a representative CLM was found to be controllable by varying the concentration of the pharmaceutical in the activating aqueous solution. The polymerization and release mechanisms did not degrade antibiotic biologic activity. CLMs may be a general class of biocompatible polymers that can locally deliver clinically useful biologics, the release kinetics of which are unaffected by the variability of implant absorption/inflammation mechanisms. © 2002 Elsevier Science (USA)

Key Words: cross-linked matrix; antibiotics; controlled release; drug delivery.

SOME DATA ANALYSIS?

Fit with Log? At long times curves should converge



FIG. 2. Release curves for tetracycline from 6 and 20% prepolymer solutions over time. Values at each time point represent percent tetracycline release (mean \pm SEM).

WOULD LOVE TO HAVE MORE DATA, R(T)

 Should be Bessel function solutions



MOLECULAR SIMULATION





CBE 60544 EVOLUTION



"WE KNOW THE EQUATIONS"



"WE KNOW THE EQUATIONS"



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ARRHENIUS KINETICS

• Most (elementary) reactions follow a temperature dependence that is called Arrhenius kinetics:

$$k = A_0 e^{-\frac{E_a}{RT}}$$

- In this equation, k is the reaction rate constant, R is the gas constant, T is absolute temperature, E_a is the activation energy and A₀ is the "pre-exponential" factor
- The exponential term tells the fraction of molecules that have enough kinetic energy to get over the reaction threshold
- A_0 is related to the rate at which molecules can rearrange internally and the number of collisions between molecules for unitary values of concentrations. It is a weak function of temperature.

REACTION RATE W/TEMP

- You may recall the generalization that reaction rates typically double for a change in temperature of 10K
- While this is a generalization, it is amazingly useful. We will explore why this is the case.

PROBABLE ORIGIN OF STATEMENT

Table 2.6 The variation in rate of a series of reactions with a 10-K change in temperature

Reaction	Temperature range, °C	Rate Change with a 10-K Temperature Change	
$CH_{3}COOCH_{2}CH_{3} + H_{2}O \xrightarrow{H^{+}} CH_{3}COOH + CH_{3}CH_{2}OH$	3.6-30.4	2.03	
$CH_3CH_2CI + NaOH \longrightarrow H_2C = CH_2 + NaCI + H_2O$	23.5-43.6	2.87	
$CH_3CH_2CH_2Cl + NaOH \longrightarrow CH_3CH = CH_2 + NaCl$	24.5-43.6	2.68	
$HPO_3 + H_2O \Longrightarrow H_3PO_4$	0-61	3.0	

Source: Data from Van't Hoff (1884).

CRICKET CHIRP RATES



Figure 2.11 The rate that crickets chirp as a function of temperature. Data for field crickets (Gryllys pennsylvanicus). From Heinrich (1993).

E-COLI GROWTH RATE



Figure 2.10 The rate of E. coli growth as a function of temperature. [Adapted from Bailey and Ollis (1977).]

TEMPERATURE EFFECTS 25

PLANT GROWTH

Table 2.7The variation in therespiration rate of plants with a10° change in temperature

Wheat	2.47
Lilac	2.48
Lupine	2.46

Source: Data from Clausen (1890).

GEOCHEMICAL REACTIONS

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RATE LAWS OF CHEMICAL REACTIONS



FIGURE 1.24. Some typical Arrhenius plots for geochemical reactions. (d) Mg tracer diffusion data for garnets normalized to 10 kbar and f_{O_2} conditions determined by the graphite- O_2 buffer. (Figure and data from Chakraborty and Ganguly 1991 and Chakraborty et al. 1992.)

REACTION TIME SCALES FOR DIFFERING ACTIVATION ENERGY



Figure 2.8 A plot of $\tau_{1/2}$ versus. E_a at 100, 200, 300, 400, and 500 K.

REACTION RATE CHANGE WITH TEMPERATURE



Figure 2.9 The fractional change in the rate of an nth-order reaction when the temperature is changed from 25 to 35°C.

CATALYZED REACTION PATHWAY



Figure 4.1.2 |

Energy versus reaction coordinate for ozone decomposition. (a) direct reaction, (b) Cl catalyzed reaction.

INDUSTRIAL CATALYSTS

Industrial catalysts operate in the same nominal rate range



Figure 2.21 Turnover numbers for some typical reactions. [From Masel (1996).]

REACTING SYSTEMS

$A \longrightarrow B$

- rate of accumulation of moles of "A" =
- rate that moles of A flow into the system -
- rate that moles of A flow out of the system
- rate at which moles of A are consumed by reaction

$$\frac{d n_A}{dt} = \dot{n}_{A,in} - \dot{n}_{A,out} - \dot{\psi}_{A,reaction}$$

$$V\frac{d C_A}{dt} = q_{in}C_{A,in} - q_{out}C_{A,out} - r_A V$$

- V - Volume of system
- q --- volumetric flow rate
- C--- concentration moles/volume
- r - reaction rate

IF NO INFLOW OR OUTFLOW

$$V \frac{d C_A}{dt} = -r_A V$$
$$\frac{d C_A}{dt} = -r_A$$
$$\frac{d C_A}{dt} = -kC_A$$

• Or a more complicated reaction term

RATE EQUATIONS

 $r_{A} = k \quad "0 \text{ order"}$ $r_{A} = kC_{A} \text{ "1st order"}$ $r_{A} = kC_{A}C_{B} \quad "2 \text{nd order"}$ $r_{A} = kC_{A}^{n}C_{B}^{m} \quad "n + m \text{ order"}$ $r_{S} = \frac{kC_{S}C_{Ez0}}{K_{B}} \text{ (Michaelis-Mention)}$

$$S = \frac{S - E_{20}}{K_m + C_s}$$
 (Michaelis-Menton)

REFERENCES FOR TODAY



Chemical Kinetics and Catalysis

Richard I. Masel

REACTION PROGRESS



EXO/ENDOTHERMIC REACTIONS

UTAPLER Z. Hate Constants of Elementary Reactions



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Figure 2.3.1 |

Potential energy profiles for the elementary reaction $A + B \rightarrow S + W$ for (a) an endothermic reaction and (b) an exothermic reaction.

RATE EQUATIONS

 $r_{A} = k \quad "0 \text{ order"}$ $r_{A} = kC_{A} \text{ "1st order"}$ $r_{A} = kC_{A}C_{B} \quad "2 \text{nd order"}$ $r_{A} = kC_{A}^{n}C_{B}^{m} \quad "n + m \text{ order"}$ $r_{S} = \frac{kC_{S}C_{Ez0}}{K_{B}} \text{ (Michaelis-Mention)}$

$$S = \frac{S - E_{20}}{K_m + C_s}$$
 (Michaelis-Menton)

RATE EQUATIONS FOR CHEMICAL REACTIONS

Table 1.4.3 [Molecularity and rates of elementary steps.

Molecularity	Number of reactant molecules	General description	Example (1)	Rate constant (1)
Unimolecular	1	$A \rightarrow \text{ products}$	$N_2O_5 \rightarrow NO_2 + NO_3$	$1.96 \times 10^{14} \exp[-10660/T], \mathrm{s}^{-1}$
Bimolecular	2	$2A \rightarrow \text{products}$ $A + B \rightarrow \text{products}$	$NO + NO_3 \rightarrow 2NO_2$	2.0×10^{11} , cm ³ /s/molecule (2)
Trimolecular (rare)	3	$3A \rightarrow \text{products}$ $2A + B \rightarrow \text{products}$ $A + B + C \rightarrow \text{products}$	$2NO + O_2 \rightarrow 2NO_2$ NO + NO ₂ + H ₂ O \rightarrow 2HNO ₂	$3.3 \times 10^{-39} \exp(530/T), \text{ cm}^{6}/\text{s/molecule}^{2}$ (2) $\leq 4.4 \times 10^{-40}, \text{ cm}^{6}/\text{s/molecule}^{2}$ (2)

1.14

(1) From J. H. Seinfeld, Atmospheric Chemistry and Physics of Air Pollution, Wiley, 1986, p. 175.

(2) Concentrations are in molecules/cm³.

UNIMOLECULAR ISOMERIZATION A-->M



Although glucose, fructose, and sucrose are all sugars, they are not equally sweet. If sucrose would be ranked as 100 on an arbitrary sweetness scale, then fructose would be 173 and glucose only 74. Therefore, products like Coke and Pepsi now use fructose in their formulations. This fructose is produced from corn. Raw corn starch is "depolymerized" and treated to yield an aqueous solution of glucose that is then converted to fructose by the enzyme glucose isomerase. The enzyme is immobilized on a ceramic support and this heterogeneous catalyst can provide greater than 18 tons of fructose per ton of catalyst.

EFFECT OF CATALYSTS

Table 2.10 The change in rate of some typical reactions seen when a catalyst is added to the reaction mixture

Reaction	Catalyst	E _a Uncatalyzed, kcal/mol	E _a , Catalyzed, kcal/mol	Rate of Enhancement Calculated at 500 K
$\frac{1}{H_2 + I_2 \rightarrow 2HI}$	Pt	44	14	1013
$2N_2O \rightarrow 2N_2 + O_2$	Au	58	29	1013
$(C_2H_5)_2O \rightarrow 2C_2H_4 + H_2O$	I_2	53	34	10 ⁸

Source: Table adapted from data in Bond (1987).

EFFECT OF CATALYST ON ENERGY PATHWAY



Figure 5.1.1 |

Schematic energy diagram for the oxidation of CO and a Pt catalyst. (From data presented by G. Ertl in Catalysis: Science and Technology, J. R. Anderson and M. Boudart, Eds., vol. 4, Springer-Verlag, Berlin, 1983, p. 245.) All energies are given in kJ mol⁻¹. For comparison, the heavy dashed lines show a noncatalytic route.

ENZYME CATALYSTS



INDUSTRIAL CATALYSTS

Table 2.9 Common Heterogeneous Catalysts

Catalyst	Reaction			
Platinum on alumina, nickel on alumina	Hydrogeneration/dehydrogenation			
Platinum/tin on acidic alumina	Reforming			
Solid acids (zeolites)	Hydrocarbon isomerization, cracking			
Silver	$C_2H_4 + \frac{1}{2}O_2 \rightarrow$ ethylene oxide			
$(B_2O_3)_{x}(MO_3)_{y}$	$CH_2 = CHCH_3 + \frac{3}{2}O_2 + NH_3 \rightarrow CH_2CH - CHO + H_2O$			
V ₂ O ₅	$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$			
Platinum gauze	$2NH_3 + 4O_2 \rightarrow N_2O_5 + 3H_2O$			

"REAL" (APPARENT) KINETICS CAN BE COMPLEX

 Table 2.11
 A selection of some of the rate equations for some common catalytic

 reactions extracted from the compilation of Mezaki and Inoue (1991)

Reaction	Catalyst	Rate Equation		
$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$	V ₂ O ₅	$\frac{k_1 K_3 K_4 P_{SO_2} P_{O_2}^{1/2} - k_2 K_5 P_{SO_3}}{1 + K_2 P_2^{1/2} + K_4 P_{SO_2} + K_5 P_{SO_3}}$		
$N_2 + \frac{3}{2}H_2 \rightarrow NH_3$	Fe/Al ₂ O ₃	$k_{1}P_{N_{2}}\left(\frac{P_{H_{2}}^{3}}{P_{NH_{3}}^{2}}\right)^{a} - k_{2}\left(\frac{P_{NH_{3}}^{2}}{P_{H_{2}}^{3}}\right)^{1-a}$		
$\rm CO + 2H_2 \rightarrow CH_3OH$	CuO/ZuO/Al ₂ O ₃	$\frac{k_1 P_{CO} P_{H_2}^2 - k_2 P_{CH_3OH}}{1 + k_3 P_{H_2} + k_4 P_{CO} + k_5 P_{CO} P_{H_3}^{3/2}}$		
$C_2H_4 + H_2 \rightarrow C_2H_6$	Ni/Al ₂ O ₃	$\frac{k_1 K_2 K_3 P_{H_2} P_{C_2 H_4}}{(1 + K_2 P_{H_2} + K_3 P_{C_2 H_4})^2}$		
$C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O$	Ag/Al ₂ O ₃	$\frac{k_1 K_2 P_{O_2} P_{C_2 H_4}}{1 + K_2 P_{O_2} P_{C_2 H_4}}$		
$\rm CO + H_2O \rightarrow H_2 + CO_2$	Fe ₂ O ₃ /Cr ₂ O ₃	$\frac{k_1 K_3 K_4 P_{CO} P_{H_2O} - k_2 K_5 K_6 P_{H_2} P_{CO_2}}{(1 + K_3 P_{CO} + K_4 P_{H_2O} + K_5 P_{CO_2} + K_6 P_{H_2})^2}$		
$4\mathrm{NH}_3 + 6\mathrm{NO} \rightarrow 5\mathrm{N}_6 + 6\mathrm{H}_2\mathrm{O}$	Pt	$\frac{k_1 K_2 K_3 P_{NO} P_{NH_3}^{1/2}}{(1 + K_2 P_{NO} + K_3 P_{NH_3}^{1/2})^2}$		

OTHER RATE EXPRESSIONS

Table 1.4.2¹ | Examples of rate functions of the type: $r = k \prod C_i^{\alpha_i}$.

Reaction	Rate function		
$CH_3CHO \Rightarrow CH_4 + CO$	k(CH ₃ CHO) ^{1.5}		
$C_2H_6 + H_2 \Rightarrow 2CH_4$ (catalytic) ShH \Rightarrow Sh $\pm \frac{3}{2}$ H	$k(C_2H_6)^{0.9}(H_2)^{-0.7}$		
$\frac{SOH_3 \Rightarrow SO + \frac{1}{2}H_2}{N_2 + 3H_2 \Rightarrow 2NH_3 (catalytic)}$	$k(SDH_3)^{2.25}$ $k(N_2)(H_2)^{2.25}(NH_3)^{-1.5}$		

¹From M. Boudart, Kinetics of Chemical Processes, Butterworth-Heinemann, 1991, p. 17.

DIFFERENT REACTOR TYPES

TABLE 2-4	TYPICAL SPACE TIME FOR INDUSTRIAL REACTORS ²			
Reactor Type	Mean Residence Time Range	Production Capacity Few kg/day to 100,000 tons/year		
Batch	15 min to 20 h			
CSTR	10 min to 4 h	10 to 3,000,000 tons/year		
Tubular	0.5 s to 1 h	50 to 5,000,000 tons/year		

TIME SCALES FOR REACTIONS

Table 2-5 shows space times for six industrial reactions and reactors.

TABLE 2-5 SAMPLE INDUSTRIAL SPACE TIMES³

		Reaction	Reactor	Temperature	Pressure atm	Space Time
	(1)	$C_2H_6 \rightarrow C_2H_4 + H_2$	PFR [†]	860°C	2	1 s
Typical industrial	(2)	CH ₃ CH ₂ OH + HCH ₃ COOH → CH ₃ CH ₂ COOCH ₃ + H ₂ O	CSTR	100°C	l	2 h
reaction space times	(3)	Catalytic cracking	PBR	490°C	20	I s < τ < 400 s
	(4)	$C_6H_5CH_2CH_3 \rightarrow C_6H_5 CH = CH_2 + H_2$	PBR	600°C	1	0.2 s
	(5)	$\rm CO$ + $\rm H_2O$ \rightarrow $\rm CO_2$ + $\rm H_2$	PBR	300°C	26	4.5 s
	(6)	$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$	CSTR	50°C	1	20 min

[†]The reactor is tubular but the flow may or may not be ideal plug flow.

SIMPLEST PROCESS ECONOMICS

- We might start with a need or desire to produce a certain mass of product per year.
- Immediately we would do a calculation on the expected revenue from such production, \$/year
- The next calculation would be cost to produce

$$\frac{\$}{yr} = \frac{\$}{kg}\frac{kg}{yr} = \frac{\$}{kg}\rho Vk$$

- in this equation r is density,V is reactor volume and k is the first order reaction constant, ''space-time'' $\sim k$
- If k is too small, then V will be too big for the process to be economical this is (at least at the moment) a problem with cellulosic ethanol.
- Note that you can increase "k" by increasing temperature, there is a limit because this can cost more (unless the reaction is very exothermic) or because the molecules decompose.

SUMMARY

- Reaction kinetics for a very wide range of reactions follow (or roughly follow) Arrhenius kinetics
- Most important biological reactions need to occur on time scales of seconds and hence have activation energies of approximately 20 kcal/mole.
 - This leads to a doubling of reaction rate in approximately 10 degrees of temperature increase
- While in general, reactions of common components can have arbitrary rates, industrial processes need to be profitable, this requires reaction rates on the order of fractions of a sec or at least not longer than minutes.
 - Thus most industrially significant reactions use a catalyst which reduces the nominal activation energy to be lower that 35-40 kcal/mole. Many typical reactions occur with an activation energy of about 25 kcal/mole. Again, in the range of typical reaction conditions, a IOC increase in temperature causes something close to a doubling of reaction rate.
- Simple process economics can be determined from just knowing the reaction rate (expressed as a first order rate constant.) If the rate is too slow, the reactor volume will be too large for the process to be profitable.