

M_t - total mass of fluid within reactor
 C_p - specific heat of fluid, energy/mass deg
 T - temperature
 t - time

$$M_t C_p \frac{dT}{dt} = V(-\Delta H) r_A(X_A, T) + q A_k \quad (\text{eqn 8.2-1})$$

~~P~~ $\frac{dT}{dt}$ $\frac{dT}{dt}$ $\frac{dT}{dt}$
309 2nd ed
F1B

Note: This equation neglects energy required to change the temperature of the reactor and internals $(m C_p)_{\text{reactor}}$

Oct 19, 2004

SPECIAL HEAT TRANSFER SITUATIONS

1. ISOTHERMAL $\frac{dT}{dt} = 0$ $T = \text{const.}$

Material and energy equations are uncoupled and may be solved separately.

2. ADIABATIC $q = 0$

~~q~~ is specified by rxn rate

$$M_t C_p \frac{dT}{dt} = V(-\Delta H) r_A(X_A, T)$$

$$r_A(X_A, T) = C_{A0} \frac{dX_A}{dt} \quad \text{constant volume}$$

$$M_t C_p \frac{dT}{dt} = V(-\Delta H) C_{A0} \frac{dX_A}{dt} = N_{A0}(-\Delta H) \frac{dX_A}{dt}$$

solving

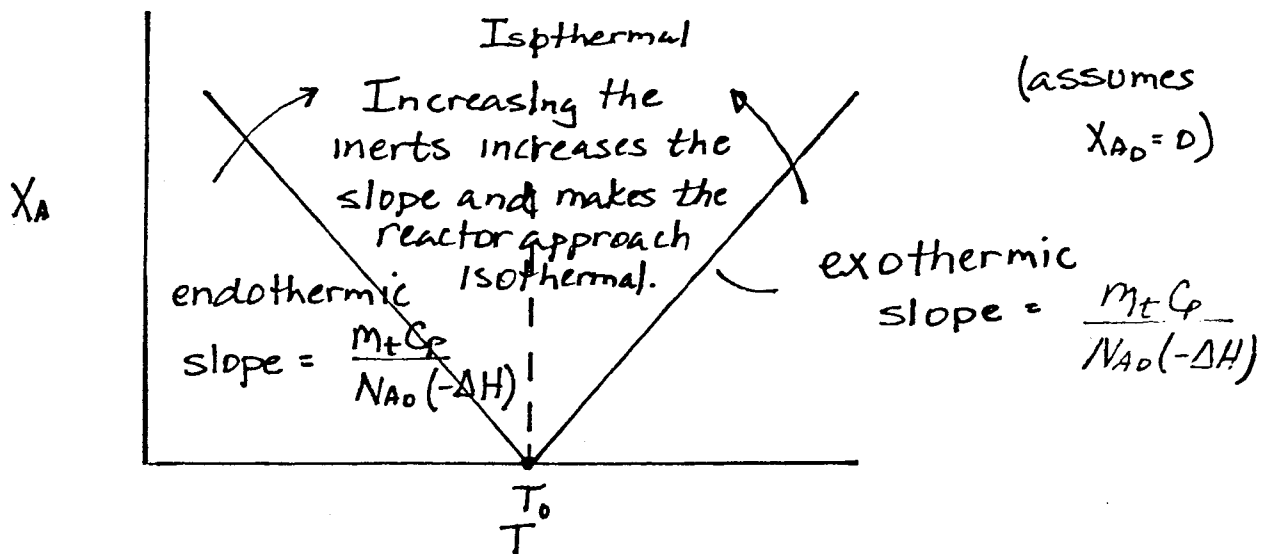
$$M_t C_p (T - T_0) = N_{A0}(-\Delta H) (X_A - X_{A0})$$

10/18/05

$$T = T_0 + \frac{N_{A0}(-\Delta H)}{m_t C_p} (X_A - X_{A0})$$

T is uniquely determined by

- (a) inlet conditions T_0, X_{A0}, N_{A0}, m_t
- (b) system properties, $-\Delta H, C_p$
- (c) fractional conversion, X_A



CONSTANT PROPERTIES

m_t - total mass - constant for a batch reactor with no phase change

C_p - specific heat of mixture - in general a function of both temperature and composition

ΔH - function of temperature

frequently the temperature, composition dependence is weak and may tend to cancel.

Thus

$$\frac{N_{A0}(-\Delta H)}{m_t C_p} = \text{const}, \text{ for many cases}$$

3. HEAT TRANSFER WITH SURROUNDINGS - heat transfer rate specified

- a) $q = \text{const.}$, independent of temp.
if the system properties are const.

$$T = T_0 + \frac{N_{A0}(-\Delta H)}{m_t C_p} (X_A - X_{A0}) + \frac{q A_t}{m_t C_p}$$

T uniquely determined by

- initial conditions, T_0, X_{A0}, N_{A0}, m_t
- system properties, $\Delta H, C_p$
- fractional conversion, X_A
- time ~~θ~~

4. TEMPERATURE IS A PRESCRIBED FUNCTION OF TIME - generally linear

$$\frac{dT}{d\theta} = m$$

$$T = T_0 + m\theta$$

again the energy and component material balance equations are uncoupled and may be solved separately.

5. GENERAL CASE - exchange with surrounding given by

$$q = U(T_r - T) \quad \begin{array}{l} T_r - \text{temp. surrounding} \\ T - \text{temp. system} \end{array}$$

numerical solution of coupled equations is required.

OPTIMAL OPERATION POLICIES

OPTIMAL TEMPERATURE - SINGLE REACTION - objective is to minimize Θ

1. IRREVERSIBLE RXN.

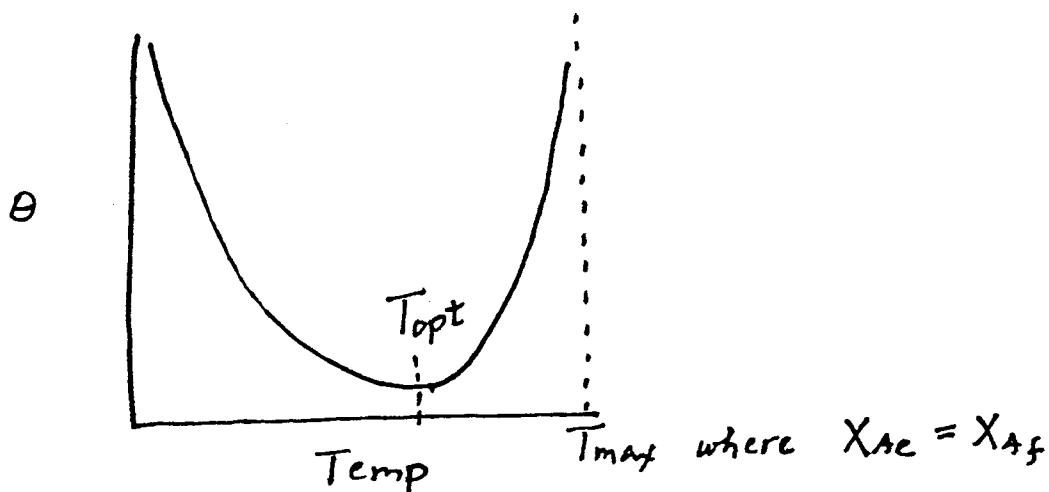
Since rate increases with temperature, the minimum Θ corresponds to $T \rightarrow \infty$. Proper operating temperature set by external constraint such as materials of construction.

2. Reversible Endothermic Reaction.

Both rate and equilibrium conversion increase with temperature. Again the minimum Θ corresponds to $T \rightarrow \infty$ and proper operating temperature set by external constraint.

3. Reversible Exothermic Reaction

Rate increases with temperature while equilibrium conversion decreases. Thus there is an intermediate optimal temperature



10/21/03

PROCEDURE for $A \rightleftharpoons R$

$$r_A = k_f C_A - k_r C_R$$

solution is (p10)

$$\tau = -\frac{1}{(k_f + k_r)} \ln\left(\frac{C_A - C_{Ae}}{C_{A0} - C_{Ae}}\right) \quad \leftarrow \text{isothermal}$$

k_f, k_r, C_{Ae} all known functions of temperature
theoretically

$$\frac{d\tau}{dT} = 0 \quad \text{solve for } T_{opt} \quad \leftarrow \begin{matrix} \text{optimum} \\ \text{isothermal} \\ \text{temperature} \end{matrix}$$

practically
solve for τ at selected temperatures
and plot results

THE METHOD OF FOURNIER and GROVES

(CHEM. ENGG., FEB. 9, 1970, p121)

graphical determination of optimal temp.
for several stoichiometries and initial conditions -

1. $A \rightleftharpoons P \quad r_A = k_f C_A - k_r C_P$

2. $A + B \rightleftharpoons P \quad r_A = k_f C_A C_B - k_r C_P$

$$\frac{C_{B0}}{C_{A0}} = 1, 1.5, 2.0 \text{ and } C_{P0} = 0$$

3. $A + B \rightleftharpoons P + S \quad r_A = k_f C_A C_B - k_r C_P C_S$

$$\frac{C_{B0}}{C_{A0}} = 1, 1.5, 2.0 \text{ and } C_{P0} = C_{S0} = 0$$

illustrate for the simplest case

$$\alpha = \frac{E_2}{E_1}$$

$$\theta_f = \text{time time}$$

Case 1) Knowing α & $\beta(\theta_f)$ can get optimal
 Case 2) knowing α & X_A

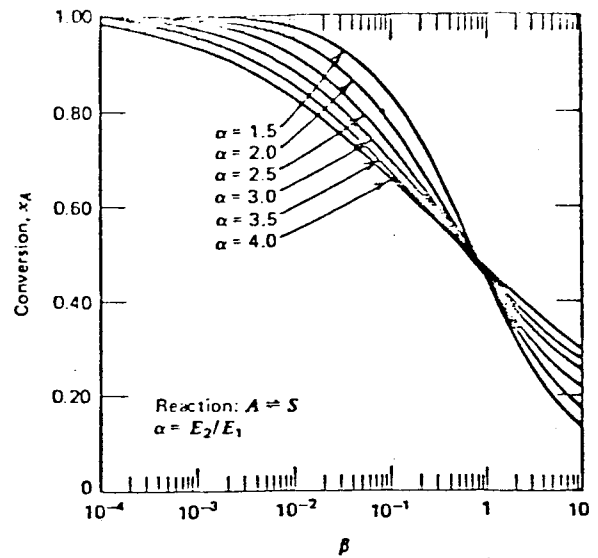
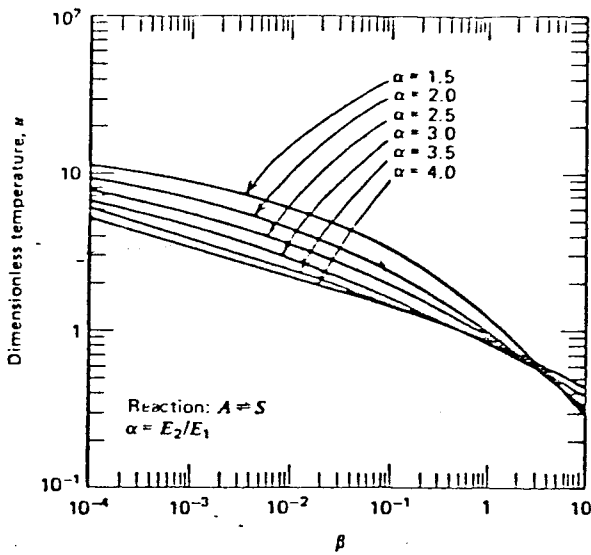


Figure 1 Dimensionless temperature versus parameter β (from Fournier and Groves [13]).

Figure 2 Conversion versus parameter β (from Fournier and Groves [13]).

Case 1) get $\tau = f(t)$

Case 1) get $X_A = f(t)$

Dimensionless quantities

$$\alpha = \frac{E_2}{E_1} \quad \text{ratio of activation energies}$$

E_2 - reverse rxn
 E_1 - forward rxn

$$\beta = \frac{\theta_f A_2}{(\theta_f A_1)^\alpha} \quad \begin{matrix} A_2, A_1 - \text{frequency factors} \\ \theta_f - \text{reaction time} \end{matrix}$$

$$u = \theta_f A_1 = \theta_f A_1 e^{-E_1/RT}$$

EXAMPLE :

$$k_f = 2.5 \times 10^5 e^{-10,000/RT} \quad (\text{hr}^{-1})$$

$$k_r = 2.0 \times 10^7 e^{-20,000/RT} \quad (\text{hr}^{-1})$$

$$X_A = 0.8$$

$$\alpha = \frac{E_2}{E_1} = 2$$

Fig 2 $X_A = 0.8 \quad \alpha = 2 \Rightarrow \beta = 8 \times 10^{-2}$

Use t & θ_f ?

$$\beta = \frac{\theta_f A_2}{(\theta_f A_1)^\alpha} = \frac{2 \times 10^7 \theta_f}{(2.5 \times 10^5 \theta_f)^2} = \frac{3.2 \times 10^{-4}}{\theta_f}$$

$$\theta_f = \frac{3.2 \times 10^{-4}}{\beta} = \frac{3.2 \times 10^{-4}}{8 \times 10^{-2}} = 4 \times 10^{-3} \text{ hr}$$

Fig 1 $\beta = 8 \times 10^{-2}$ $\alpha = 2 \Rightarrow U = 2.5$

$$U = \theta_f A_1 e^{-E_1/RT}$$

$$-\frac{E_1}{RT} = \ln \frac{U}{\theta_f A_1}$$

$$T_1 = \frac{-E_1}{R \ln \left(\frac{U}{\theta_f A_1} \right)}$$

$$= \frac{-10,000}{1.987 \ln \left(\frac{2.5}{4 \times 10^{-3} (2.5 \times 10^5)} \right)}$$

$$T_{opt} = 840^\circ \text{K}$$

Oct 21, 2004

OPTIMAL TEMPERATURE TRAJECTORY - ★

- objective is to control the temperature at each point in the reactor so that the rate is always at its maximum possible value

$$\frac{\partial r_A}{\partial T} = 0 \quad \text{at each instant in the reactor}$$

EXAMPLE (from Levenspiel)



$$k = 3 \times 10^7 e^{-11,600/RT}$$

$$\ln K = \frac{18000}{RT} - 24.7$$

$$C_{A0} = 1 \text{ mol/liter} \quad C_{R0} = 0$$

$$T_{\text{max}} = 95^\circ\text{C} \quad (\text{outside constraint})$$

$$X_{Af} = 0.8$$

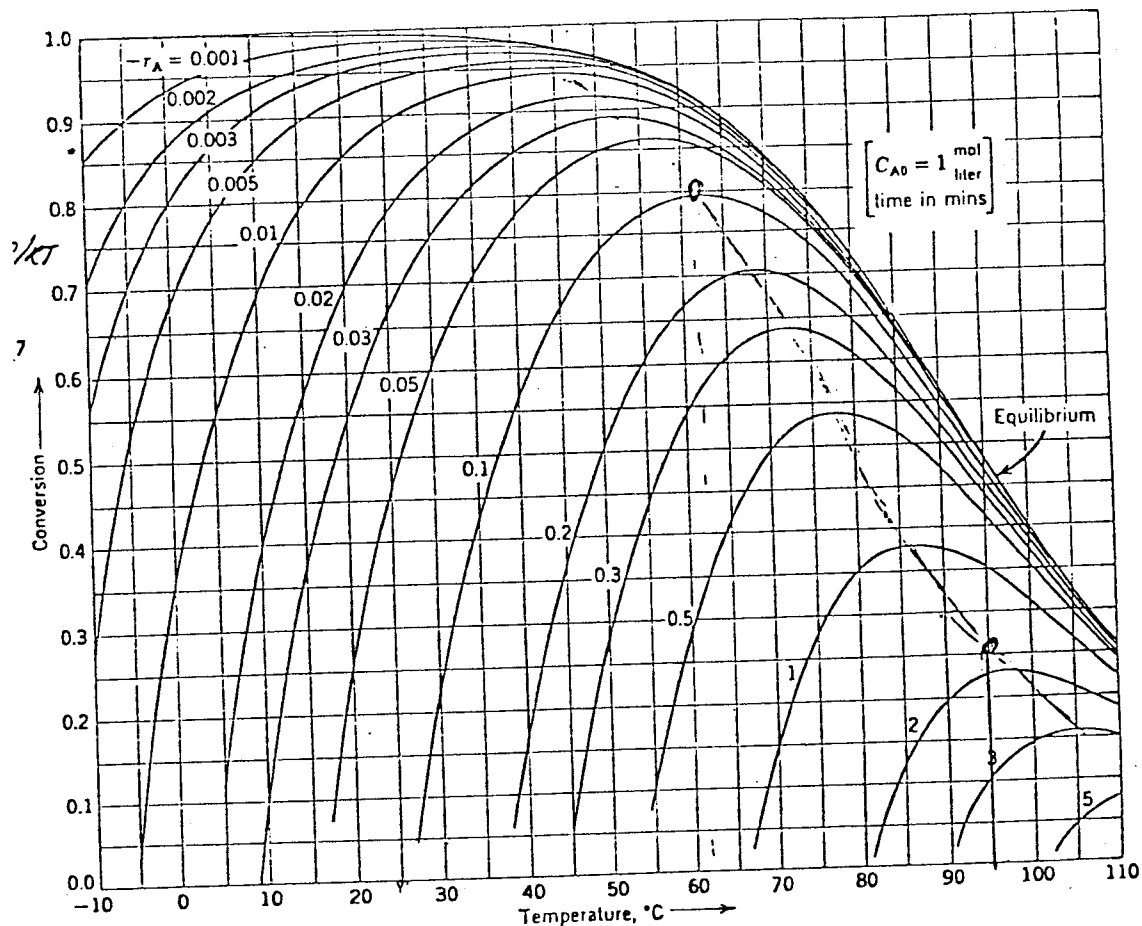
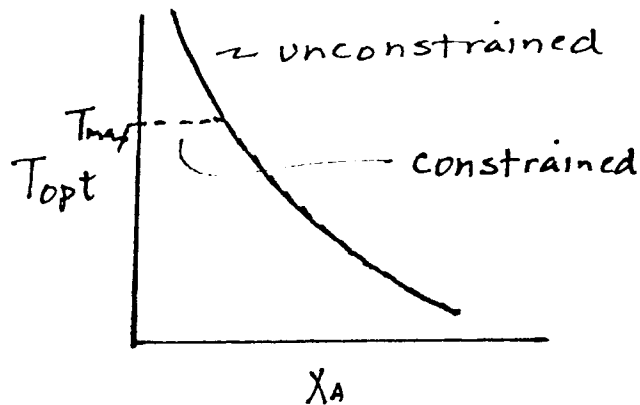


FIGURE E2.

Procedure: Fix r_A , calculate X_{Af} for selected values of T . Repeat for various values of r_A .

Result might look something like



High initial temperature to take advantage of high rate when system is far from equilibrium
 Gradually lower the temperature to take advantage of improved equilibrium yields.

Numerical integration required to determine reaction time

$$\theta_{min} = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{r_A(X_A, T_{opt}(X_A))}$$

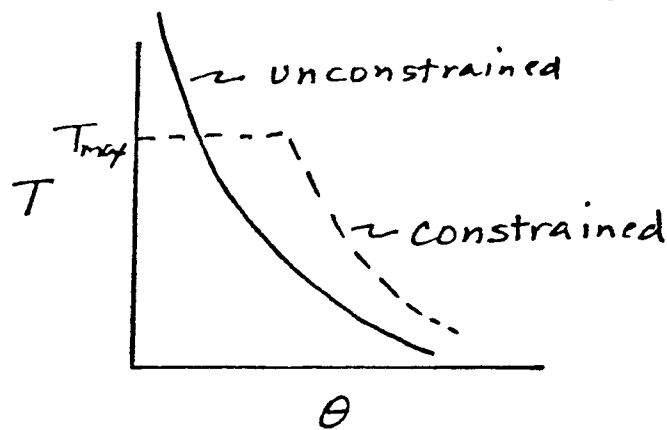
if we are constrained to $T = T_{max}$ for $0 \leq X \leq X_c$

$$\theta_{min} = C_{A0} \int_0^{X_c} \frac{dX_A}{r_A(X_A)} + C_{A0} \int_{X_c}^{X_{Af}} \frac{dX_A}{r_A(X_A, T_{opt}(X_A))}$$

isothermal-
-analytic

variable temp
- numerical

Result might look something like



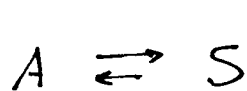
In general the chart will not be available.
Fournier and Groves (Chem. Eng., 71, No. 13, 157 (1970))
have addressed that problem also

$$T_{opt} = \left\{ \frac{1}{(-B_1)} \ln [B_2 B_3] \right\}^{-1}$$

$$B_1 = (E_1 - E_2) / R$$

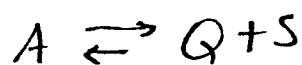
$$B_2 = A_2 E_2 / A_1 E_1$$

B_3 depends upon the particular reaction



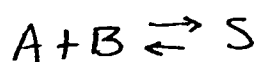
$$B_3 = \frac{X_A}{1 - X_A}$$

$$C_{S0} = D$$



$$B_3 = \frac{C_{A0} X_A}{1 - X_A}$$

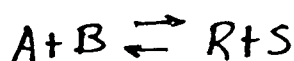
$$C_{Q0} = C_{S0} = D$$



$$B_3 = \frac{X_A}{C_{A0}(1 - X_A)(M - X_A)}$$

$$M = \frac{C_{B0}}{C_{A0}}$$

$$C_{S0} = D$$



$$B_3 = \frac{X_A^2}{(1 - X_A)(M - X_A)}$$

$$C_{R0} = D$$

Adiabatic
reactor
Example

Example:

Take rxn $A \rightarrow B$

$$r = kC_A$$

$$k = 0.8 \text{ hr}^{-1} \text{ at } 163^\circ\text{C}$$

$$E = 28960 \text{ cal/mole}$$

$$\Delta H_r = -83 \text{ cal/gr}$$

$$HW = 250 \text{ gr/mole}$$

$$C_p = 0.5 \text{ cal/gr}^\circ\text{K}$$

$$\rho = 0.9 \text{ g/cm}^3$$

How long to react 97% conv? $T_0 = 163^\circ\text{C}$

Heat Balance:

$$T = T_0 + \frac{N_A \Delta H (-\Delta H)}{mT C_p} (\chi_A - 0)$$

Basis: ~~1 mole A~~ 1 mole A

$$T = 436^\circ\text{K} + (83 \text{ cal/gr}) \times \frac{250}{mT} \times \frac{1}{0.5 \text{ cal/gr}^\circ\text{K}}$$

$$mT = 1 \text{ mole} \times 250 \text{ gr/mole} = 250 \text{ gr}$$

$$T = 436^\circ\text{K} + (83 \text{ cal/gr}) \times \frac{250 \text{ gr/mole} \times 1 \text{ mole}}{0.5 \text{ cal/gr}^\circ\text{K} \times 250 \text{ gr}}$$

$$T = 436^\circ\text{K} + 166^\circ\text{K}$$

Assumptions:

$$k_m \left(\frac{T_1}{T_2} \right) = - \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

436 → 2
 166 → 3
 14576 → 4
 2.61 × 10⁴ → 5

$$\ln\left(\frac{R}{r}\right) = -\frac{28960}{1.987} \left(\frac{1}{T} - \frac{1}{436}\right)$$

$$k = 2.61 \times 10^4 e^{-14570/T}$$

Design eqn: $cost \propto V$

$$T = C_{A0} \int_{X_A}^{1} \frac{dX_A}{-r_A}$$

$$T = C_{A0} \int_{X_A}^0 \frac{dX_A}{k(C_{A0}(1-X_A))}$$

$$T = \int_{X_A}^0 \frac{dX_A}{k(1-X_A)}$$

$$T = \int_{X_A}^0 \frac{dX_A}{2.61 \times 10^4 e^{-14570/436+166X_A} (1-X_A)}$$

X_A	Integrand	ΔX_A (Integrand) / μs
0	1.248	0.048
0.05	1.204	0.028
1	1.407	0.10
2	1.147	0.27
3	0.58	0.04
4	0.25	0.02
5	0.12	0.01
6	0.06	0.01
8	0.03	0.01
97	0.005	0.001

use spreadsheet
 get better
 result

$$S = 1.173 \text{ hr}$$

Conversion, Time, & Temp Relationship

X_A	t	T
0	0	436
.05	.049	444
.1	.077	453
.2	.104	469
.3	.114	486
.4	.118	502
.5	.120	519
.6	.121	535
.8	.122	529
.87	.123	597

$\Delta T = 161^\circ K$