Prof. Shankar
Lec. 20 8/11/2012 1/1

Advanced Reaction Engineering

Temperature Effects on Rate + Equilibria

Thursday
8 NOV. 12
1400 - 1500.

a) If ΔH is + ve and $T > 298$ K we

get $\ln K/K_{298} > 0$ implying K

increases as T increases.

b) ΔH - ve and $T > 298$ K then

$\ln K/K_{298} < 0$ and so implying

K decreases as T increases

Temperature Effects on Rate + Equilibria

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad \ldots (1)$$

Called Vant Hoff's Equation

Also

$$RT \ln K = - \Delta G^{\circ} \quad \ldots (2)$$

If ΔH is not a strong function of T we get

$$\ln \frac{K}{K_{298}} = \frac{(-\Delta H)}{R}\left[\frac{1}{T} - \frac{1}{298}\right]$$

Example

$$A \underset{2}{\overset{1}{\rightleftarrows}} B$$

Let us say $r_1 = k_1 C_A$ and $r_2 = k_2 C_B$

$$r_B = r_1(+1) + r_2(-1) = r_1 - r_2$$

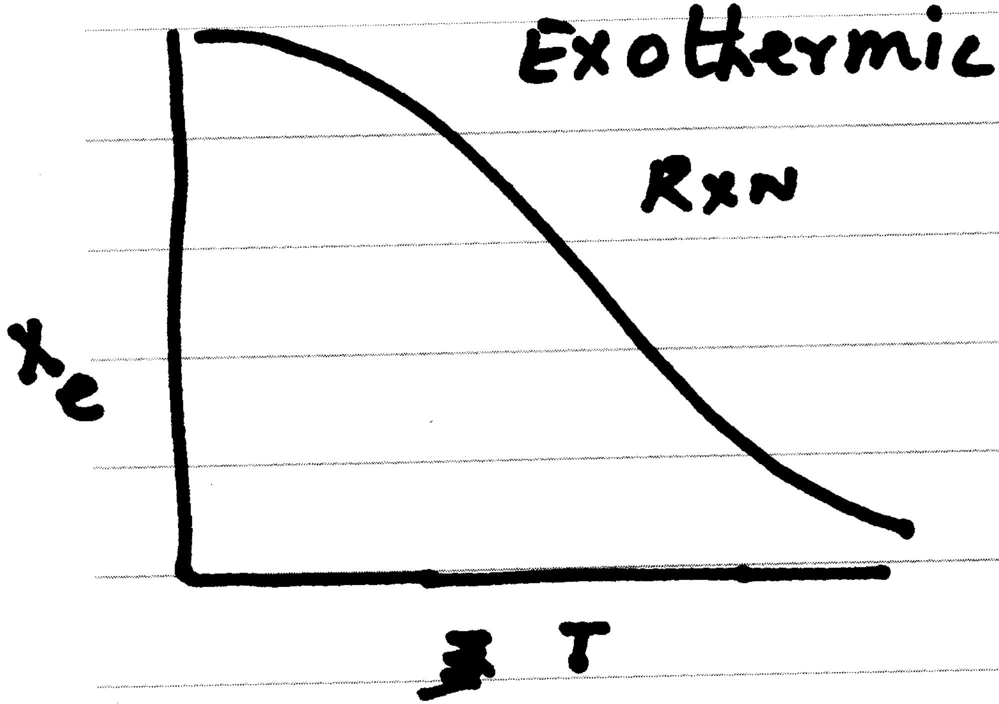
$$= k_1 C_A - k_2 C_B = k_1 C_{A0}(1-x) - k_2 C_{A0} x$$

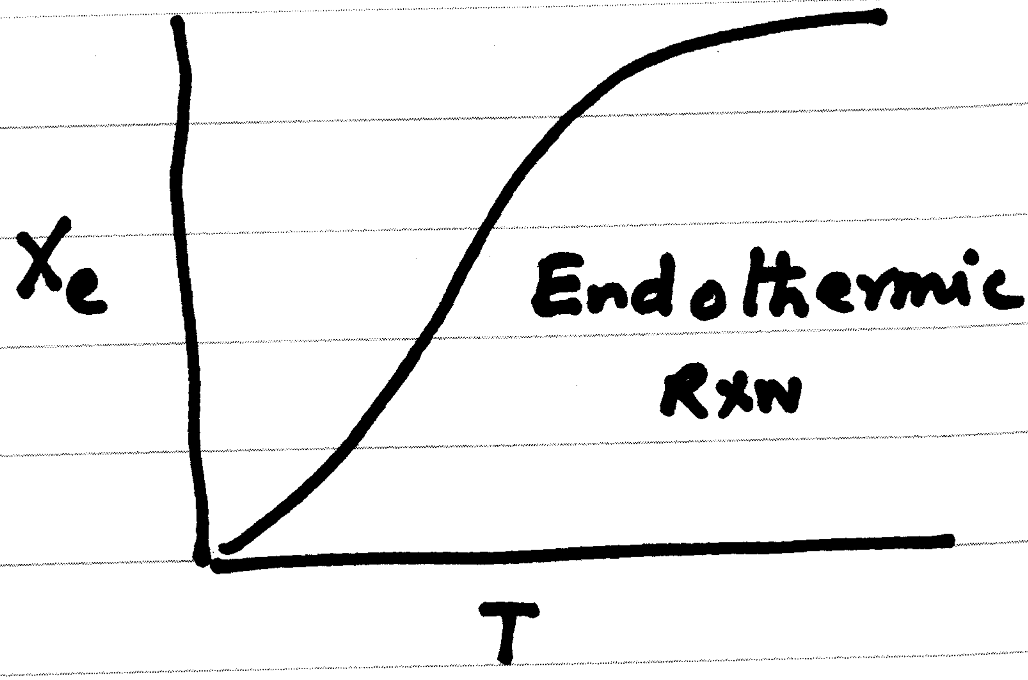
at Equilibrium $r_B = 0$

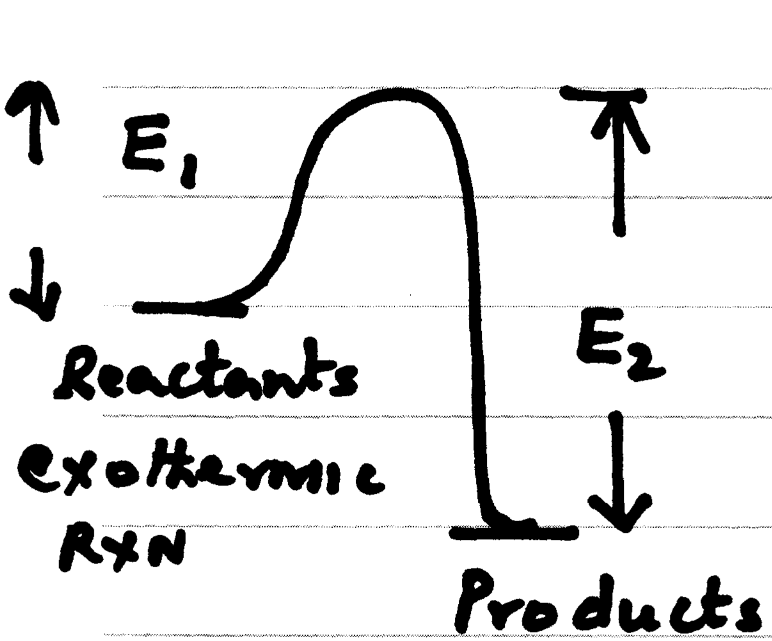
$$0 = k_1 C_{A0}(1-x_e) - k_2 C_{A0} x_e \Rightarrow \frac{x_e}{1-x_e} = \frac{k_1}{k_2} = K$$

or $x_e = K/(K+1)$

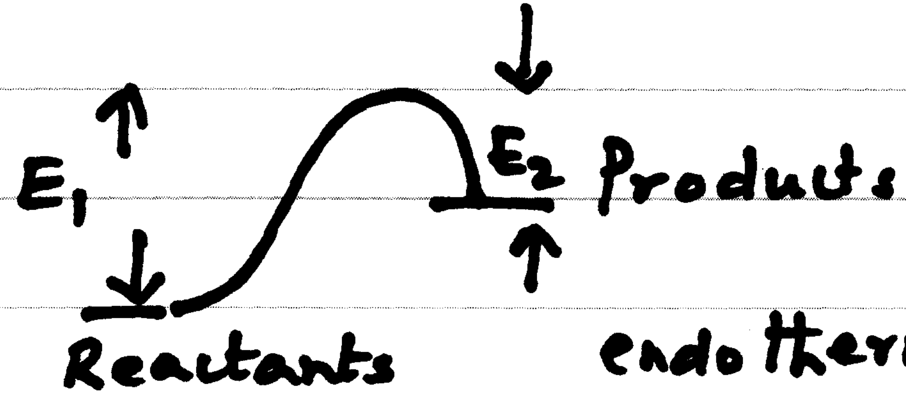
$$X_e = K/(K+1) = \frac{1}{(1+1/K)}$$







exothermic RxN



endothermic RxN

$$\Delta H = E_1 - E_2$$

So for exothermic since $E_2 > E_1$; ΔH is $-ve$

endothermic since $E_2 < E_1$; ΔH is $+ve$

$$r_B = k_1 C_A - k_2 C_B$$

$$= k_{10} e^{-E_1/RT} C_{A0}(1-x) - k_{20} e^{-E_2/RT} C_{A0} x$$

$$k_{20} e^{-E_2/RT} \left[\frac{k_{10}}{k_{20}} e^{-(E_1-E_2)/RT} \cdot C_{A0}(1-x) - C_{A0} x \right]$$

$$r_B = k_{20} e^{-E_2/RT} \left[\frac{k_{10}}{k_{20}} e^{-\Delta H/RT} C_{A0}(1-x) - C_{A0} x \right]$$

$$r_B = k_{20}\, e^{-E_2/RT}\left[\frac{k_{10}}{k_{20}}\, e^{-\Delta H/RT}\, C_{A0}(1-x) - C_{A0}x\right]$$

Endothermic RXN (at constant x)

$k_{20}\, e^{-E_2/RT}$ increases as T increases

$e^{-\Delta H/RT}$ increases as T increases.

So r_B (for endothermic rxn) increases as T increases

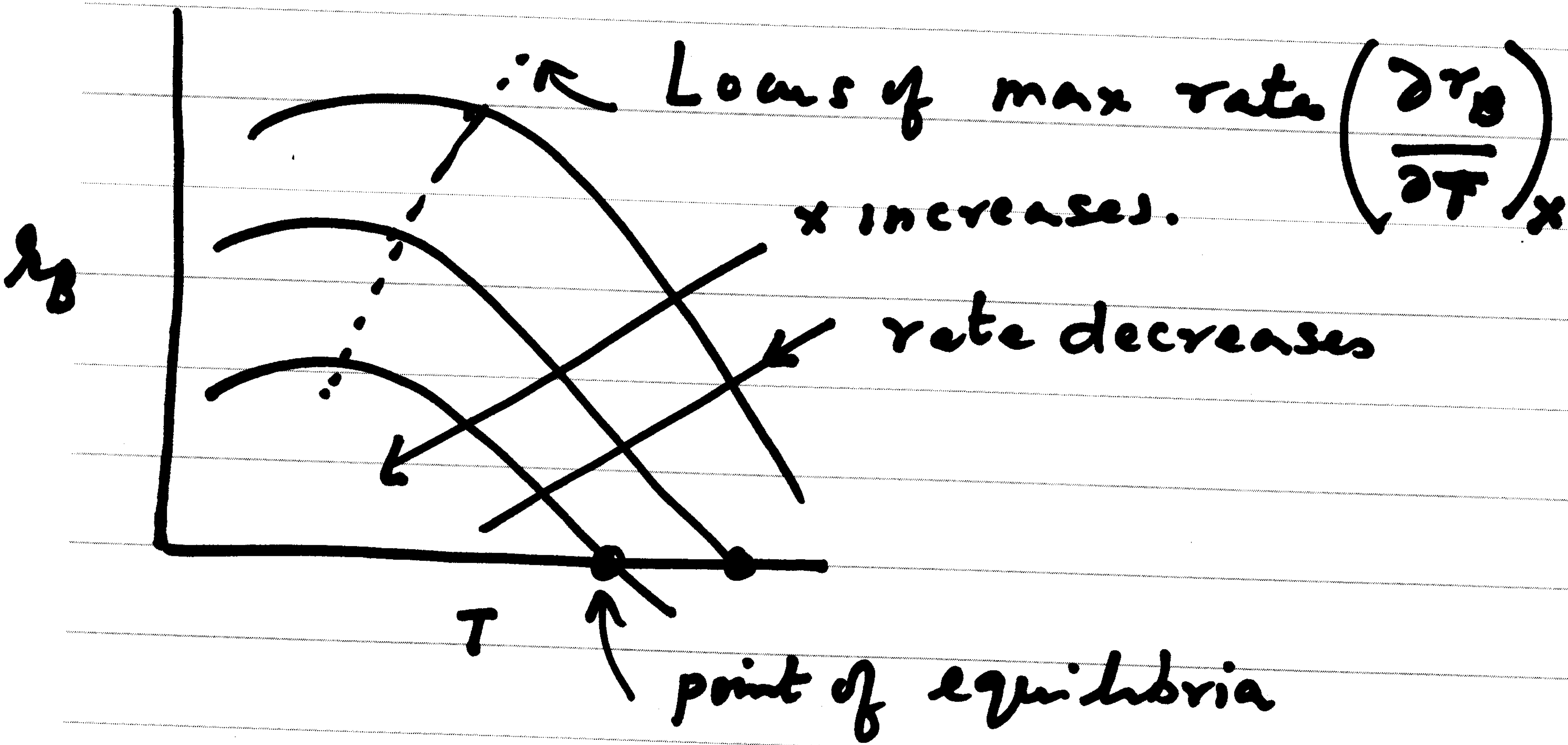
$$r_B = k_{20} e^{-E_2/RT} \left[\frac{k_0}{k_{20}} e^{-\Delta H/RT} C_{A0}(1-x) - C_{B0}\, x \right]$$

Exothermic Rxn at Constant x

$k_{20} e^{-E_2/RT}$ increases as T increases

$e^{-\Delta H/RT}$ decreases as T increases.

So r_B goes through a maxima. So exothermic reaction there is a maxima for each x. This is Curve of locus of max rates.


Locus of max rate $\left(\frac{\partial r_B}{\partial T}\right)_x$
x increases.
rate decreases
r_B
T
point of equilibria

Therefore for each x there is a temperature at which r_B takes max value. So it is necessary to find the eqn to locus of max rates and also to see what strategies might be possible so as to make it possible to operate along the locus of max rates.

Determination of locus of max rates

$$r_B = k_1 C_{A0}(1-x) - k_2 C_{A0}\, x$$

$$\left(\frac{\partial r_B}{\partial T}\right)_x = \frac{k_1 E_1}{RT^2} C_{A0}(1-x)_m - \frac{k_2 E_2 C_{A0}\, x_m}{RT^2} = 0$$

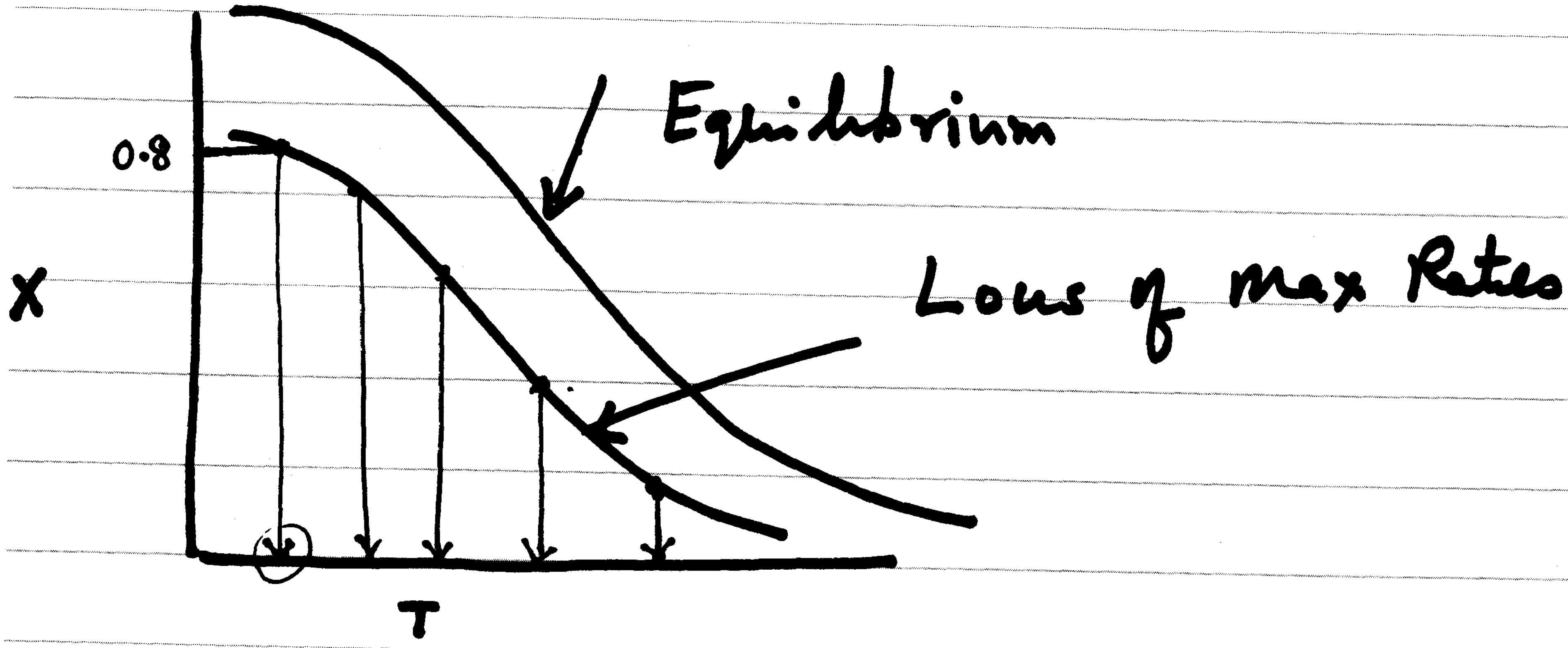
$$\frac{1-x_m}{x_m} = \frac{k_1 E_1}{k_2 E_2} = \frac{K\, E_1}{E_2}$$

gives the equation to locus of max rates.

$$X_e = K/(1+K) = 1/(1+1/K)$$

and $$X_m = \frac{K\delta}{1+K\delta} \quad \text{or} \quad \frac{1}{(1+1/K\delta)}$$

where $\delta = E_1/E_2$ <1 for Exothermic rxns



$X_e = 1/(1 + 1/K)$ and $X_m = \dfrac{1}{(1 + 1/K\delta)}$

Since $\delta < 1$ X_m–T Curve always lies below X_e – T curve

Operating on the Locus of Max Rates (CSTR)

single independent rxn & at steady state

Design Eqn:

$$\frac{F_{A0}\,X}{-r_A} = V \qquad -(1)$$

$$V C_p \cancel{\frac{dT}{dt}} = v_0\, C_p\,(T_0 - T) + \sum_{i=1}^{p=1} (r_1 - r_2)(-\Delta H_1^{*})$$

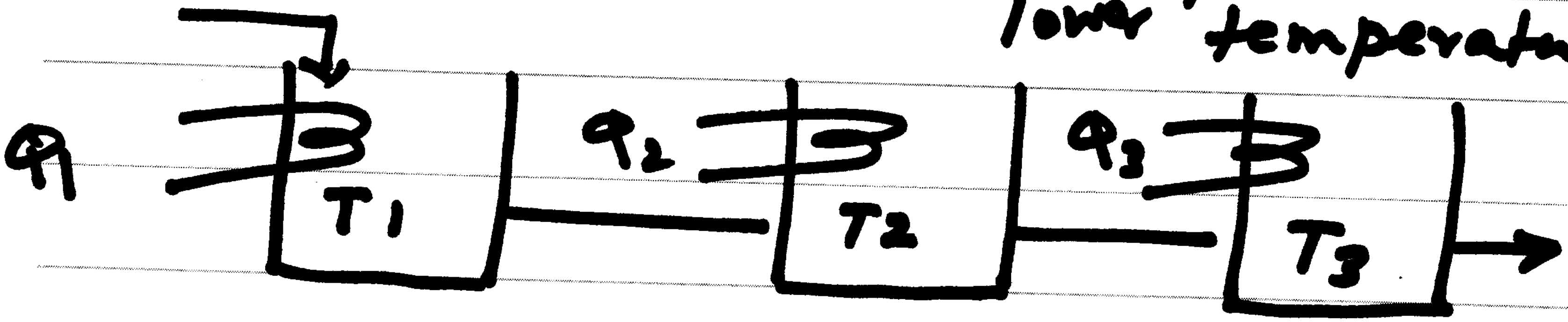
$$+ Q - W_s \qquad -(2)$$

$$\frac{X_m}{1 - X_m} = \frac{K\delta}{1 + K\delta} \quad \left(\text{where } \delta = \frac{E_1}{E_2}\right) \quad --(3)$$

Eqn (1), (2), (3) define the coordinates of the design. Typically if X_m is specified then Eqn (3) yields T of operation; Eqn (1) specifies residence time; and Eqn (3) specifies Q the heat load to be managed.

a) A multistage CSTR operates on the lines.

b) Reaching higher conversions require operation at lower + lower temperatures.



Multistage PFR.? Why?

Lets consider $A \rightleftarrows B$

Design Eqn

$$v C_p \frac{dT}{dV} = (r_1 - r_2)(-\Delta H_1^*) + \cancel{q} - \cancel{W_s} \quad -(1)$$

For an adiabatic PFR; no work output

$$F_{A0} \frac{dx}{dV} = (r_1 - r_2) \quad --(2)$$

From (1) + (2)

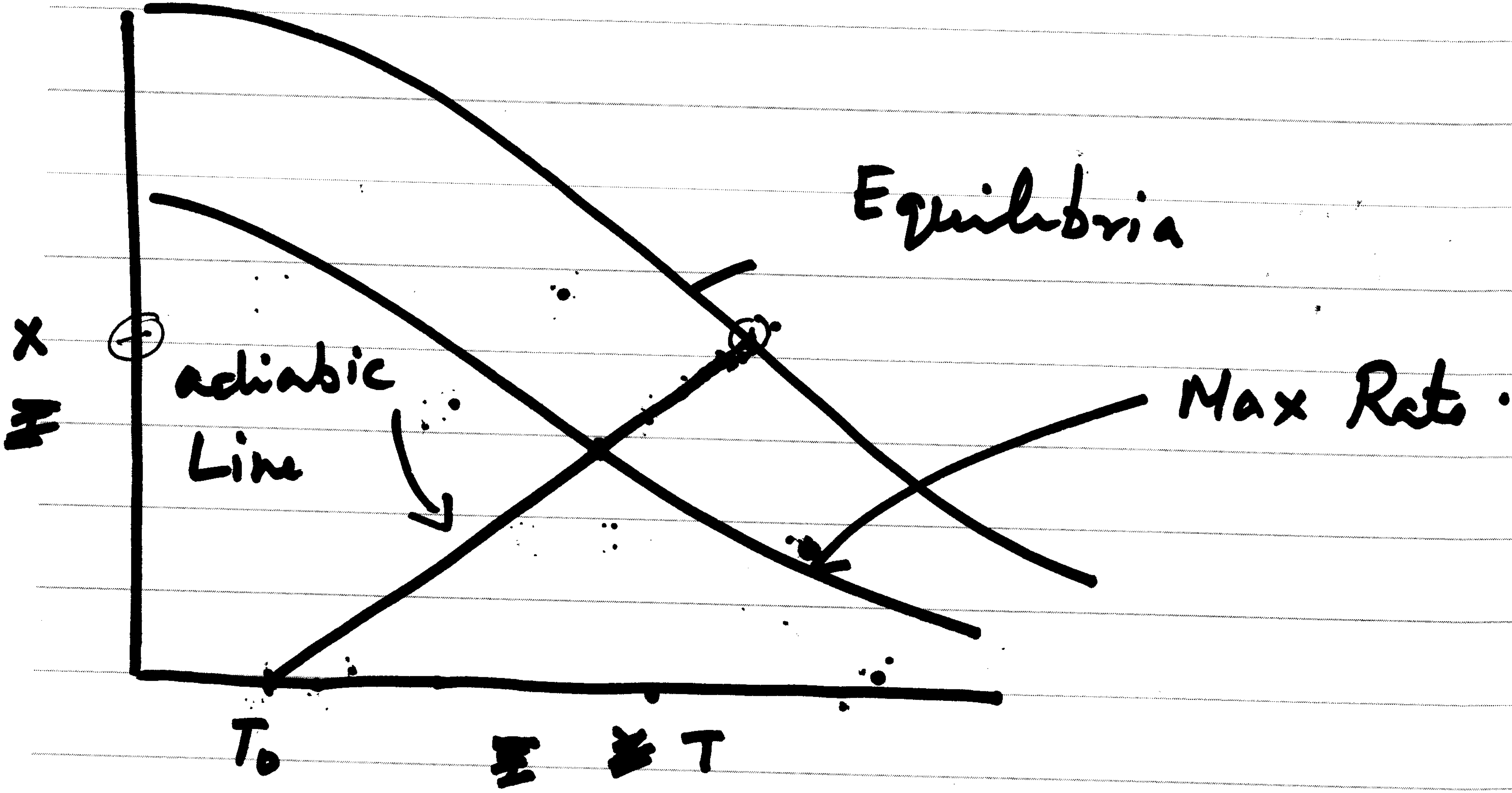
$$\boxed{\frac{v C_p}{F_{A0}} \frac{dT}{dx} = (-\Delta H_1^*)}$$

$$\frac{dT}{dx} = \frac{(-\Delta H_1^*)\, F_{A0}}{v\, C_p} = C_{A0} J \text{ (say)}$$

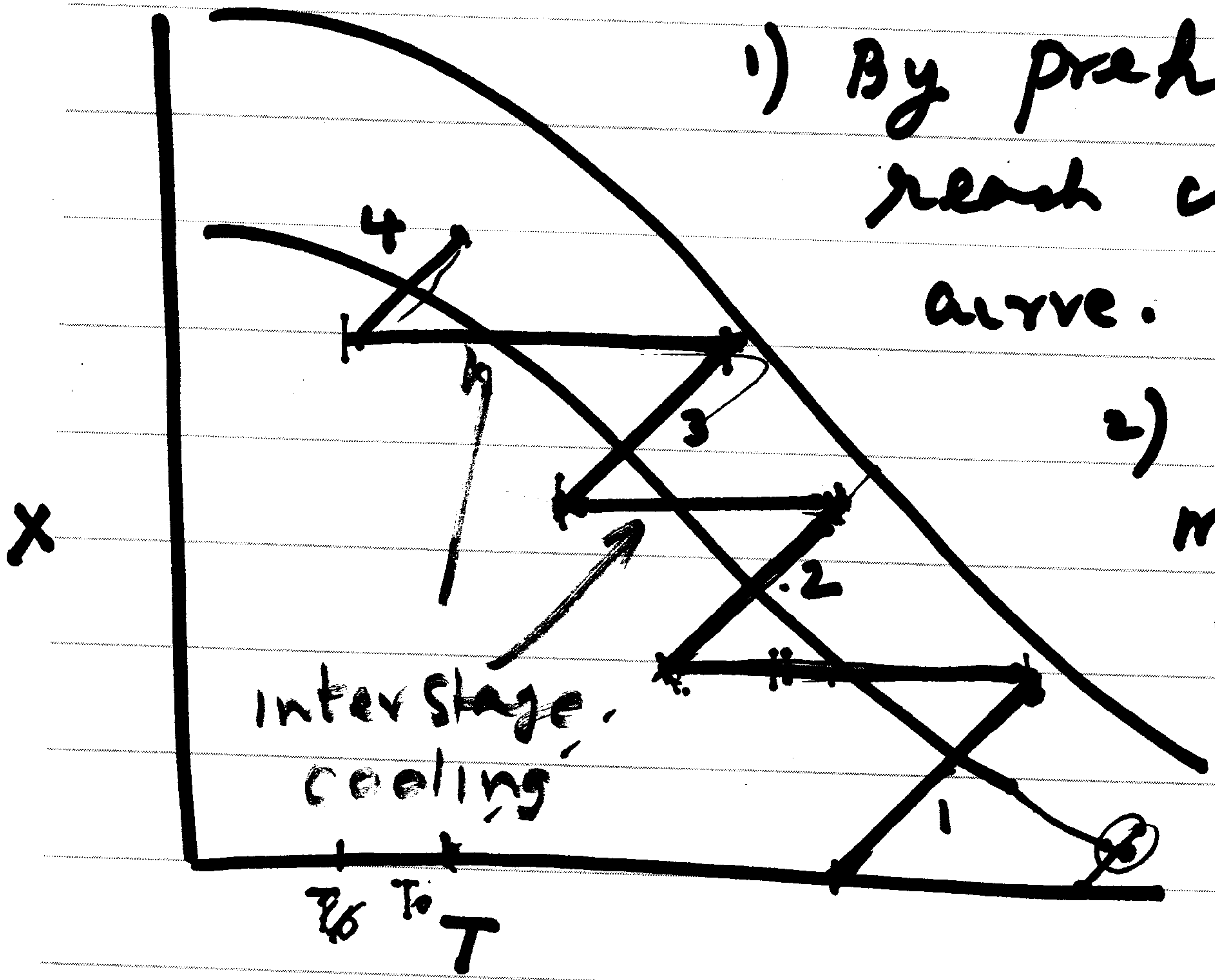
$$\frac{-\Delta H_1^*}{C_p} = J.$$

If J is a constant then dT/dx is a st. line. If $v \equiv v_0$ then we can write

$$\frac{dT}{dx} = (-\Delta H_1^*)\, \frac{C_{A0}}{C_p} = C_{A0} J. \text{ (say)}.$$



Starting at T_0 we move along st line of slope J. We stop where rate becomes so low that it is not worth going further.



1) By preheating feed, we reach closer to Max Rate curve.

2) By staying close to max rate curve we get average rates close to max rates to be achieved.

3) Interstage cooling enable multistage operation to achieve X desired

Further discussion on temperature Effects

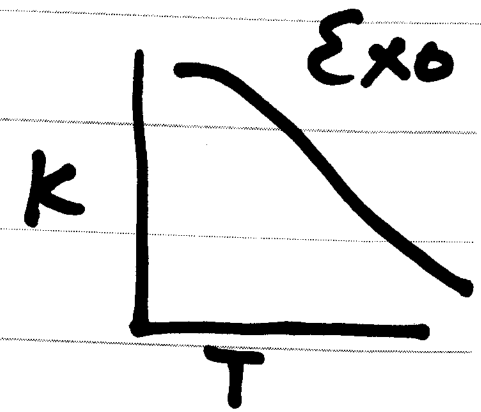
$$\gamma (r_B) = k_1 C_{A0} (1-x) - k_2 C_{A0} x \quad - (1)$$

$$\left(\frac{\partial r_B}{\partial T}\right)_x = 0 \Rightarrow \frac{1-X_m}{X_m} = K \frac{E_1}{E_2}$$

$$\Rightarrow X_m = \frac{K E_1/E_2}{1 + K E_1/E_2} \quad - (2)$$

We now want to see how contours of ~~constant~~ $\left(\frac{\partial x}{\partial T}\right)_{r_B}$ look and what we can learn from these curves

Let $r_B = \gamma$ (constant)



$$\gamma = k_1 C_{A0}(1-x) - k_2 C_{A0}\, x$$

$$\frac{\gamma}{k_1 C_{A0}} = 1 - x - \frac{x}{K} = 1 - \frac{x(K+1)}{K}$$

$$\boxed{x = \left(1 - \frac{\gamma}{k_1 C_{A0}}\right)\left(\frac{K}{K+1}\right)} \quad - - \quad (3)$$

$$K = \frac{k_1 \nearrow}{k_2 \nearrow}$$

$$X = \left(1 - \frac{\gamma}{K_1 C_{A0}}\right)\left(\frac{K}{K+1}\right) \quad \text{... (1)}$$

$\left(1 - \frac{\gamma}{K_1 C_{A0}}\right)$ increases as T increases

and $K/(K+1) = \left(\frac{1}{1+1/K}\right)$ decreases

as T increases. So $X-T$ curve will

show a maxima at each γ_B. Let us

find this maxima

point of maxima $\left(\frac{\partial x}{\partial T}\right)_{\gamma_B} = 0$? $\quad X = \left(1 - \frac{\gamma}{k_1 C_{A0}}\right)\left(\frac{K}{K+1}\right)$.

$$(d\ln K)/dT = \frac{\Delta H}{RT^2}$$

$$\frac{dK}{dT} = \frac{K\,\Delta H}{RT^2} \quad \text{and} \quad \frac{dk_1}{dT} = \frac{k_1 E_1}{RT^2}$$

$$\left(\frac{\partial x}{\partial T}\right)_{\gamma_B} = 0 = \frac{\gamma k_1 E_1}{k_1^2 C_{A0} RT^2}\,\frac{K}{K+1} + \left(1 - \frac{\gamma}{k_1 C_{A0}}\right)\left[\frac{1}{K+1} - \frac{K}{(K+1)^2}\right]\frac{dK}{dT}$$

$$0 = \frac{\gamma k_1 E_1}{k_1^2 C_{A0} RT^2}\,\frac{K}{K+1} + \left(1 - \frac{\gamma}{k_1 C_{A0}}\right)\left[\frac{1}{(K+1)^2}\right]\frac{K\,\Delta H}{RT^2}$$

$$0 = \frac{\gamma E_1}{k_1 C_{A0} R T^2} \frac{K}{K+1} + \left(1 - \frac{\gamma}{k_1 C_{A0}}\right) \frac{K}{(K+1)^2} \frac{\Delta H}{R T^2}$$

$$0 = \frac{\gamma E_1}{k_1 \cancel{E_1} C_{A0}} + \left(1 - \frac{\gamma}{k_1 C_{A0}}\right) \frac{\Delta H}{\cancel{E}\,(K+1)}$$

$$0 = \frac{\gamma}{k_1 C_{A0}} \left(E_1 - \frac{\Delta H}{K+1}\right) + \frac{\Delta H}{K+1}$$

$$\boxed{\frac{\gamma}{k_1 C_{A0}} = \frac{-\;\Delta H/(K+1)}{\left(E_1 - \frac{\Delta H}{K+1}\right)}}$$

$$\frac{\gamma}{K_1 C_{A0}} = \frac{-(E_1 - E_2)}{E_1(K+1) - (E_1 - E_2)} \qquad \because \Delta H = E_1 - E_2$$

$$\frac{\gamma}{K_1 C_{A0}} = \frac{E_2 - E_1}{E_1 K + E_2} \quad . \quad (5)$$

$$\boxed{1 - \frac{\gamma}{K_1 C_{A0}} = \frac{E_1 K + E_2 - E_2 + E_1}{E_1 K + E_2} = \frac{E_1 (K+1)}{K.E_1 + E_2} \quad - \quad (6)}$$

From (3)

$$\left(\frac{\partial X}{\partial T}\right)_{\tau_B} = 0$$

$$X = \left(1 - \frac{\gamma}{k_1 C_{A0}}\right) \frac{K}{K+1}$$

Substituting for $\left(1 - \frac{\gamma}{k_1 C_{A0}}\right)$ from (6)

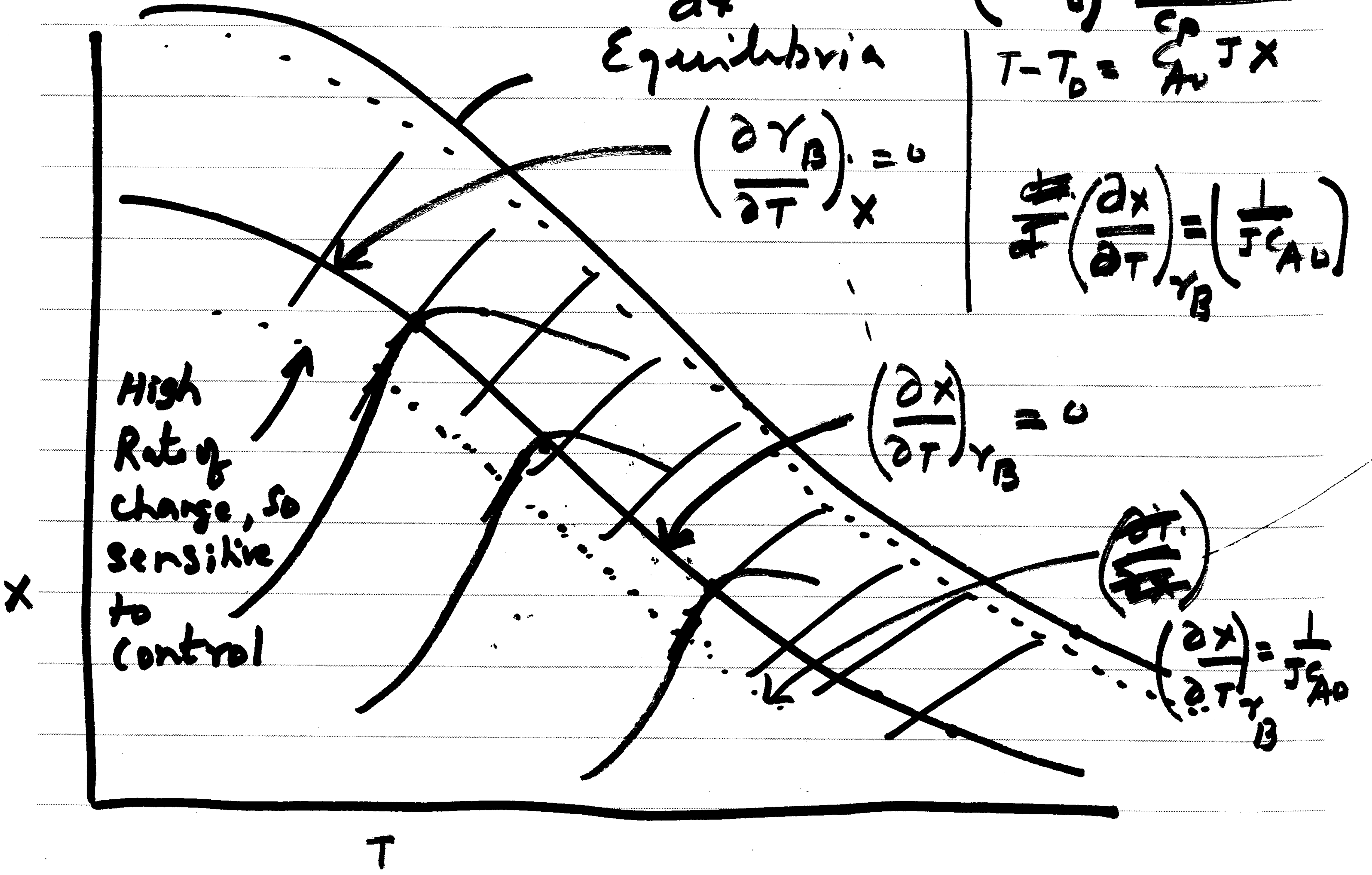
$$X = \frac{E_1 (K+1)}{(K E_1 + E_2)} \frac{K}{(K+1)} = \frac{E_1 (K+1)}{(K E_1 + E_2)} \cdot K$$

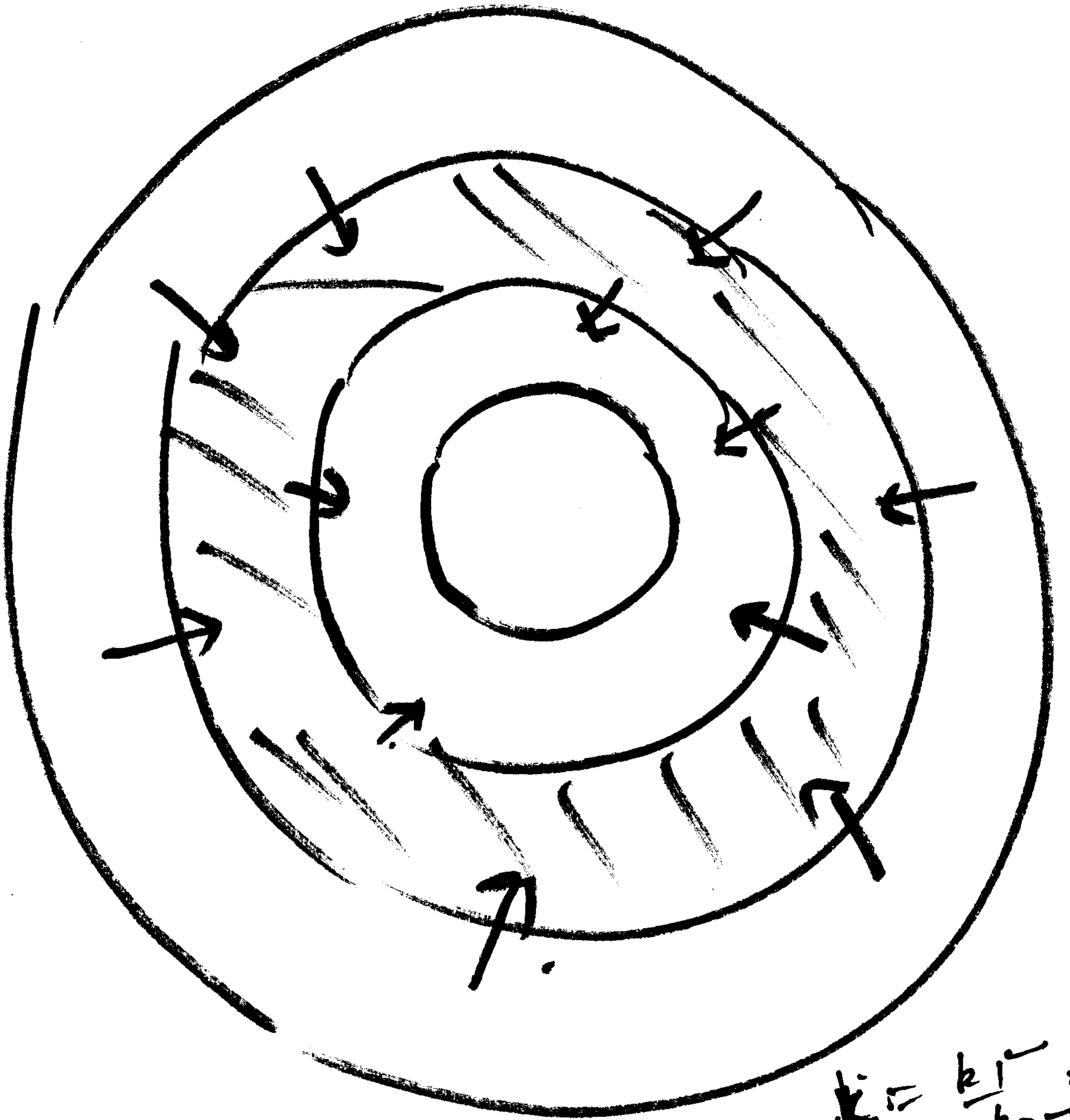
$$X = \frac{K E_1}{K E_1 + E_2} = \frac{K (E_1 / E_2)}{(K E_1/E_2 + 1)} = \frac{K \delta}{(1 + K\delta)}$$

∂r $\quad \frac{dT}{dx} = J C_{A0}$

$$(T - T_0) = \frac{C_{A0}(-\Delta H)X}{c_p}$$

$$T - T_0 = C_{A0} J X$$





$k_1 = \frac{k_1}{k_2} = 2$

$\left(1 - \frac{r}{k_1 C_{01}}\right)$ $\left(\frac{K^{k_1/k_2}}{1+K}\right)$

$\left(\frac{K}{K+1}\right)$

$5/10 = 1/2$

$5.1/10.5$

$\ominus$