28/3-18 Föreläsning 3

Jämviktsprocesser

Steam reforming

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

Water gas shift (WGS)

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Haber-Bosh

$$3H_2 + N_2 \rightleftharpoons 2NH_3$$

X-T diagram

$$A \underset{k_b}{\overset{k}{\rightleftharpoons}} B$$

$$-r_A = kC_A - k_bC_B$$

$$r = kC_A - k_bC_B$$

jmv. konst.: $K_c = \frac{k}{k_b} \Rightarrow k_b = \frac{k}{K_c}$

$$K_c = \Pi (P_{je})^{\nu_j}$$

$$K_c = \Pi (C_{je})^{\nu_j}$$

$$-r_A = kC_A - \frac{k}{K_c}C_B = k\left(C_A - \frac{C_B}{K_c}\right)$$

$$r_A = \underbrace{-kC_A}_{\text{reagerar A}} + \underbrace{\frac{kC_B}{K_c}}_{\text{produceras B}}$$

jmv.: $r_A = 0 \Rightarrow C_{Ae} - \frac{C_{Be}}{K_c} = 0 \Rightarrow C_{Ae} = \frac{C_{Be}}{K_c}$

$$C_{Ae} = C_{A_0}(1 - X_e)$$

$$C_{Ae} = \frac{C_{Be}}{K_e} = \frac{C_{A_0} X_e}{K_e} \Big\} \text{ e-jmv.}$$

$$\Rightarrow \frac{C_{A_0} X_e}{K_e} = C_{A_0}(1 - X_e) \Rightarrow \frac{X_e}{K_e} = 1 - X_e$$

$$X_e = \frac{K_e}{1 + K_e} \quad \text{och } K_e \text{ beror av temp.}$$

Gibbs fria energi : $\Delta G = \Delta H - T\Delta S$

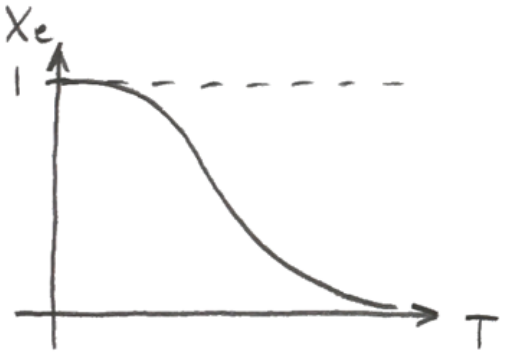
$$\Delta G = -RT \ln K_e$$

$$\Delta H - T\Delta S = -RT \ln K_e$$

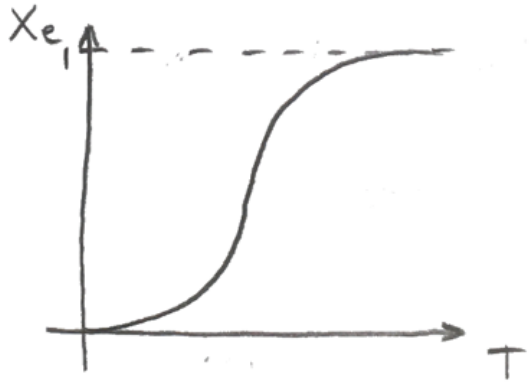
$$\Rightarrow K_e(T) \Rightarrow X_e$$

EX. $A \leftrightarrow B$, $K_e = \frac{C_B}{C_A}$ (här höjer man upp med stökiom. koeff)

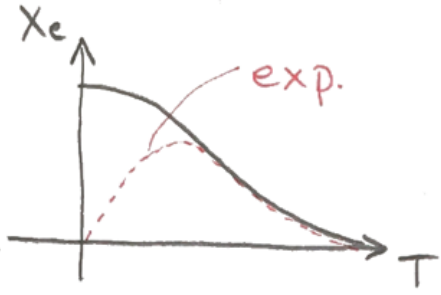
Exoterm



Endoterm



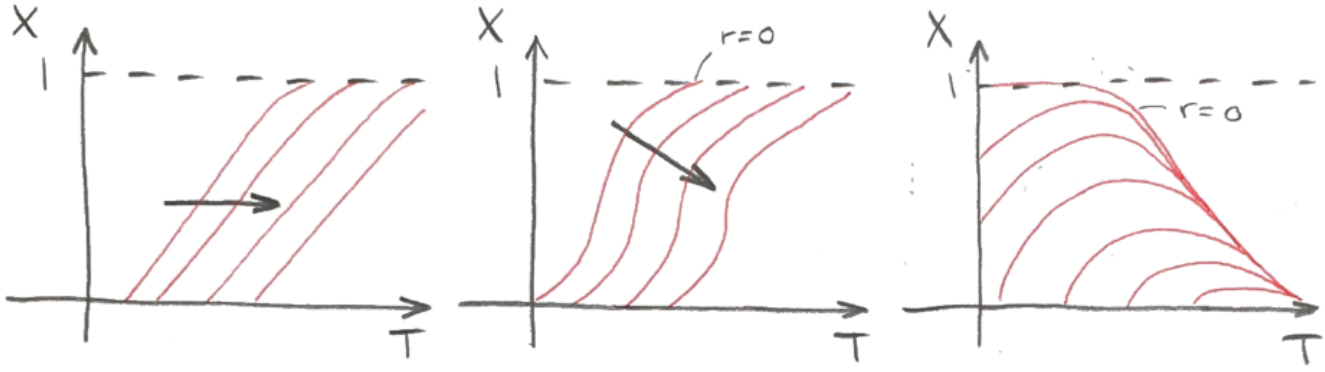
Ex. NO oxidation



$$NO + \frac{1}{2} O_2 \rightleftharpoons NO_2$$

Ens kurva kan ligga under den "generella" men aldrig över.

Konturer m. konst. r



Irreversibel | Reversibel endoterm | Reversibel exoterm

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

$$r = k_f C_{A_0}(1-X) - k_B C_{A_0} X$$

C_A C_B

$$r = \underbrace{A_f e^{-E_f/RT} \cdot C_{A_0}(1-X)}_{r_f} - \overbrace{A_b e^{-E_b/RT} \cdot C_{A_0} X}^{r_b}$$

$r = f(X, T)$

aktiverings energi

Arrhenius - $k = A e^{-E/RT}$

pre. exp. faktor

$$\left(\frac{dX}{dT}\right)_r = -\left(\frac{dr}{dT}\right)_X \Big/ \left(\frac{dr}{dX}\right)_T \quad \text{(bevis i app.)}$$

$$\left(\frac{dr}{dT}\right)_X = \frac{E_f}{RT^2}\cdot \underbrace{A_f C_{A_0}(1-X)e^{-E_f/RT}}_{r_f} - \frac{E_b}{RT^2}\underbrace{A_b C_{A_0} X e^{-E_b/RT}}_{r_b}$$

$r = r_f - r_b$

$$\left(\frac{dr}{dT}\right)_X = \frac{1}{RT^2}\left(E_f r_f - E_b r_b\right)$$

$$\left(\frac{dr}{dX}\right)_T = -C_{A_0}k_f - C_{A_0}k_b$$

$$\boxed{\left(\frac{dX}{dT}\right)_r = \frac{E_f r_f - E_b r_b}{RT^2 C_{A_0}(k_f + k_b)}} \quad *$$

* Lutningen för kurvan i X-T diagramen.

Endoterm

$E_f > E_b \Rightarrow$ E positiv

Om $r \geq 0 \Rightarrow r_f \geq r_b$

$r = r_f - r_b$, $E_f r_f > E_b r_b$

* $\left(\frac{dr}{dT}\right)_X$ ökar m. temp.

$$\left(\frac{dX}{dT}\right)_r > 0$$

$r = k_f C_{A_0}(1-X) - k_b C_{A_0} X$

$$\Rightarrow \quad X = \frac{(k_f C_{A_0} - r)}{C_{A_0}(k_f + k_b)}$$

$\left(\frac{dX}{dT}\right)_r \longrightarrow 0$ när $T \longrightarrow \infty$

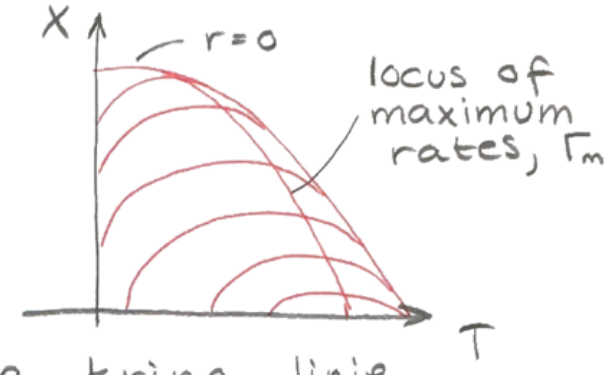
Exoterm

$$\left(\frac{\partial X}{\partial T}\right)_r = \frac{\left(\frac{\partial r}{\partial T}\right)_X}{C_{A_0}(k_f + k_b)} = \frac{E_f r_f - E_b r_b}{RT^2 C_{A_0}(k_f + k_b)}$$

$\left(\frac{\partial X}{\partial T}\right)_r$ är proportionell mot $\left(\frac{\partial r}{\partial T}\right)_X$

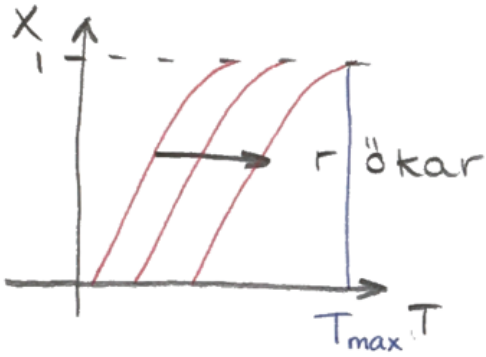
när T ökar så ändras r:

1) r ökar
2) Maximum där $\left(\frac{\partial r}{\partial T}\right) = 0$
3) Minskar



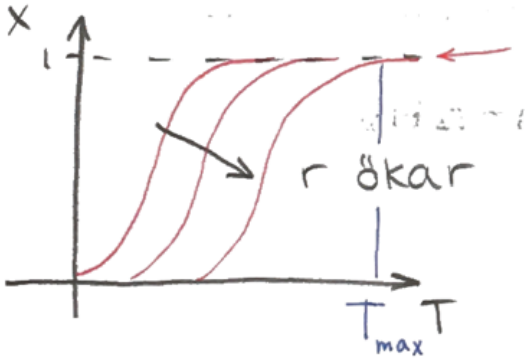
Minimera en reaktor, vara kring linje.

Irreversibel



T_{max}:
- ekonomi för värmning
- hållbarhet

Reversibel endoterm



Adiabatisk driftlinje

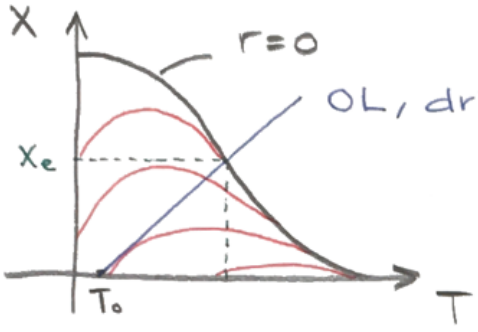
VB: $$X_A = \frac{-\sum F_{i0} \int_{T_0}^{T} C_{pi}\, dT}{F_{A0}\, \Delta H_R}$$

Antar C_p konstant

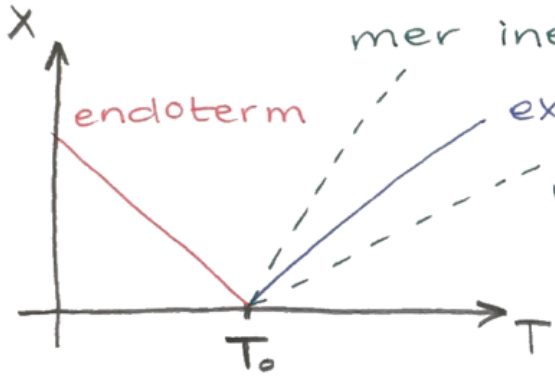
$$X_A = \frac{-\sum F_{i0}\, \tilde{C}_{pi}\, (T - T_0)}{F_{A0}\, \Delta H_R}$$

} operating line, OL (driftlinje)

Exoterm



lutning på driftlinjen: $$\frac{\sum F_{i0}\, \tilde{C}_{pi}}{F_{A0}\, (-\Delta H_R)}$$

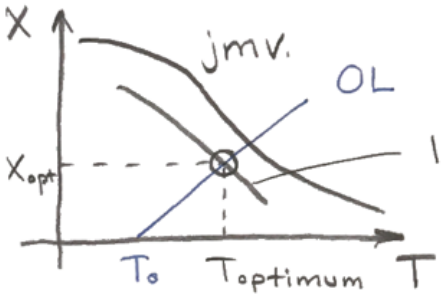


$A \rightleftharpoons B$

inert, I

$$\frac{F_{A0} C_{pA} + F_{B0} C_{pB} + F_{I0} C_{pI}}{F_{A0}\, (-\Delta H_R)}$$

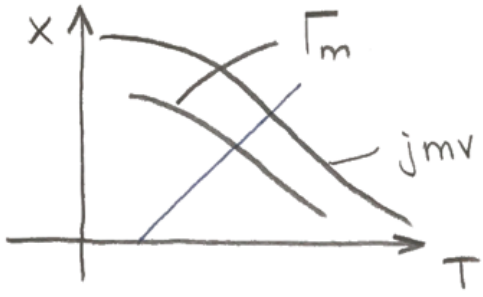
Minimera reaktorstlk.



locus of max ratos ?

TANK

TUB



Kring Γ_m

TANK

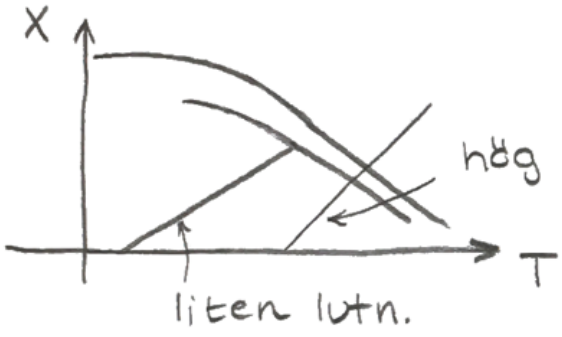
Exoterm : Locus of max rates.

Endoterm : T_{max}

TUB

Exoterm : Högsta medel r
Kring Locus of max rates

Endoterm: T_{max}

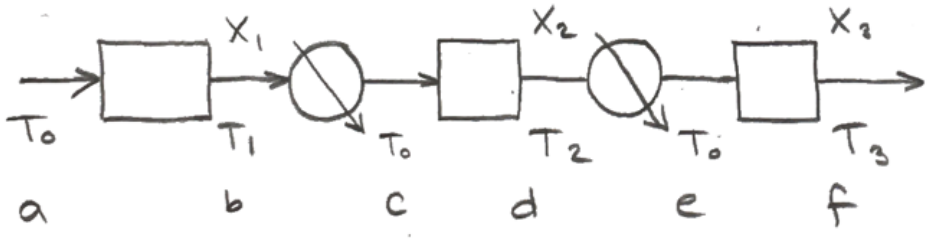


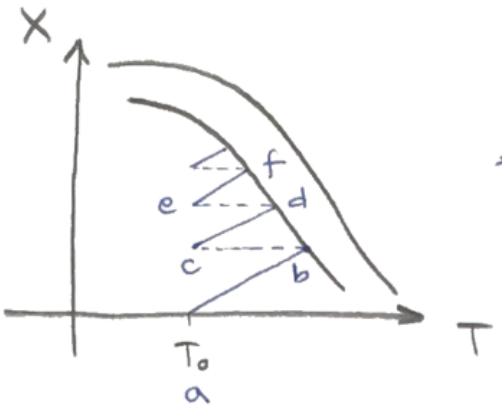
hög lutn., kan en tub anv.

Tank

Tub m. mycket recirkulation

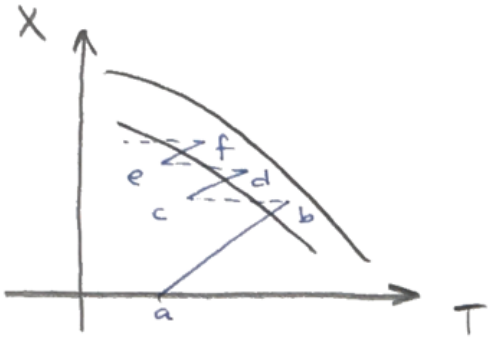
Multipla reaktorer





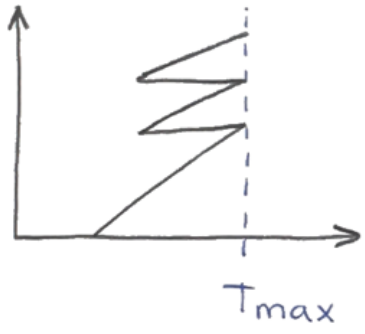
← tank, exoterm

Tub:

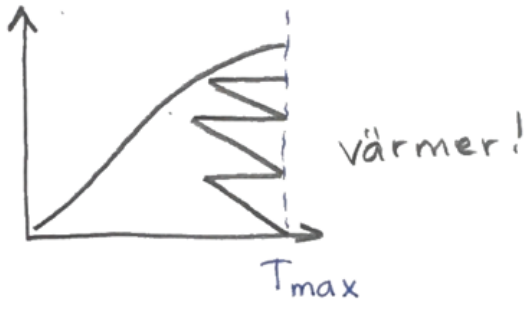


Kommentar:
Endast exoterm har locus

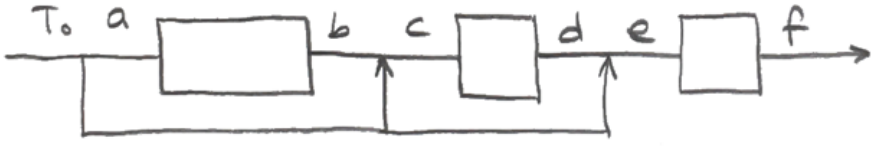
Irreversibel exoterm



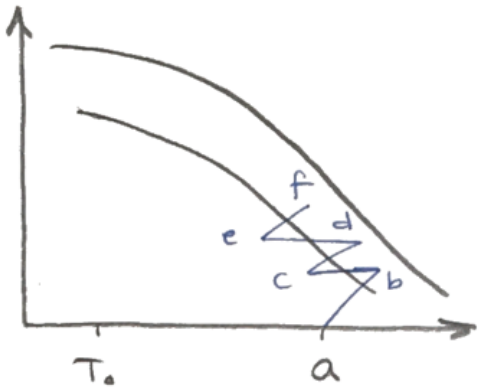
Reversibel endoterm



Cold-shot



Inflödet är väldigt kallt och ist. för att anv. en kylare, kyler man mha inflödet.



Tänk på: de vågräta linjerna är inte helt raka utan har en lutning.