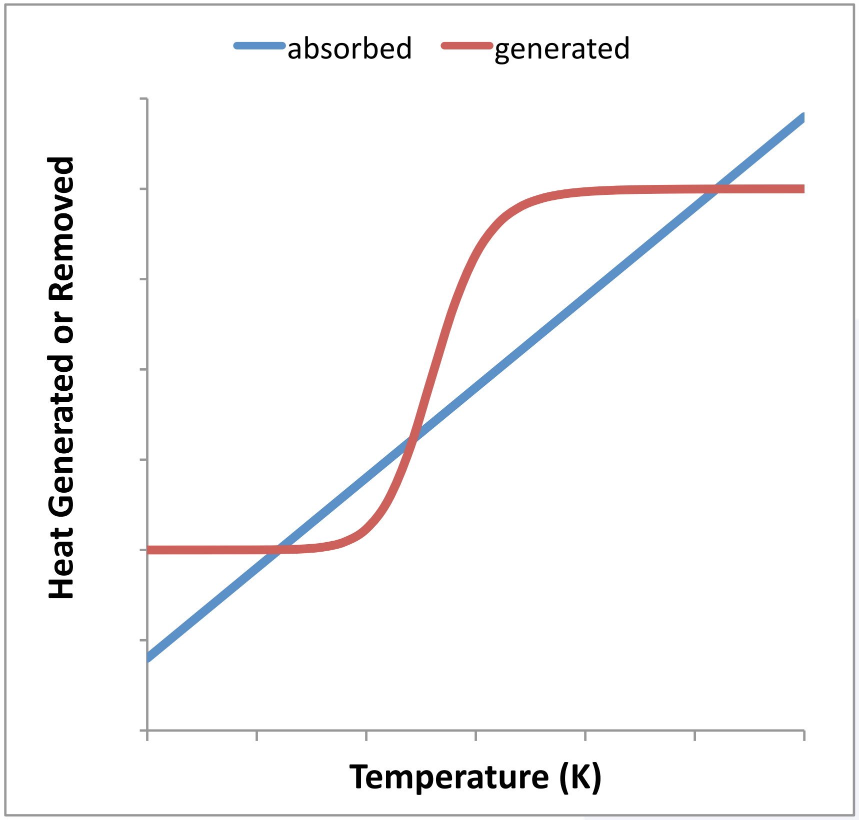
A First Course on Kinetics and Reaction Engineering

Class 25 on Unit 24

Where We're Going

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
- Part III - Chemical Reaction Engineering
  - A. Ideal Reactors
  - B. Perfectly Mixed Batch Reactors
  - C. Continuous Flow Stirred Tank Reactors
    - 21. Reaction Engineering of CSTRs
    - 22. Analysis of Steady State CSTRs
    - 23. Analysis of Transient CSTRs
    - 24. Multiple Steady States in CSTRs
  - D. Plug Flow Reactors
  - E. Matching Reactors to Reactions
- Part IV - Non-Ideal Reactions and Reactors

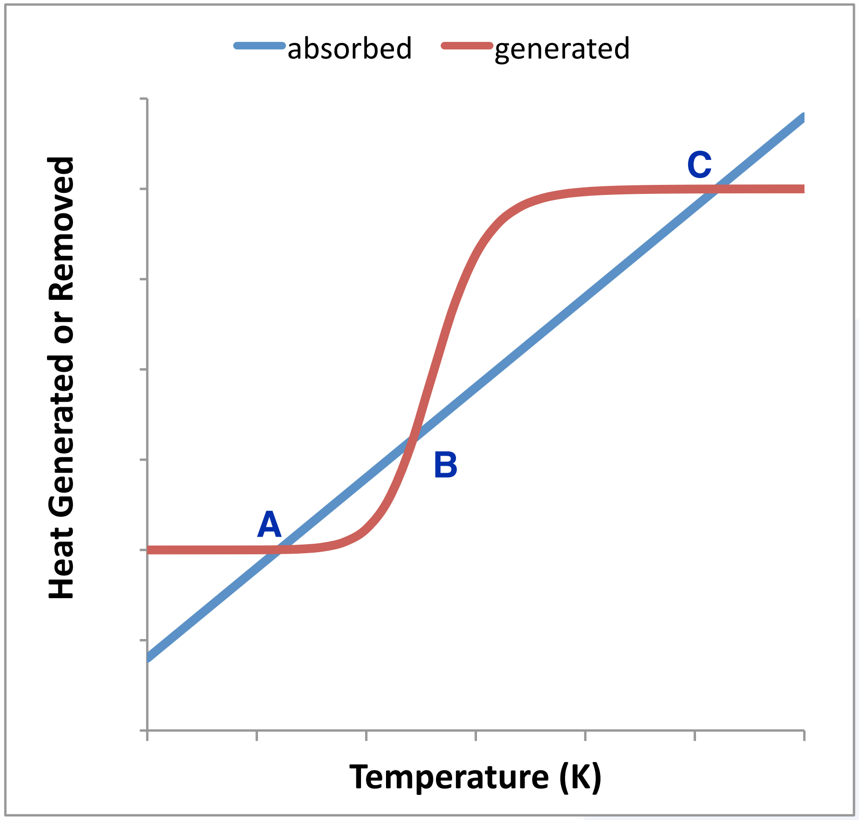
Satisfying the Steady State CSTR Energy Balance



- Choose an outlet temperature, solve the mole balance design equations, use results to compute two parts of the energy balance, plot the results
- Energy balance is only satisfied at temperatures where the two curves intersect
- In this case there are three solutions to the steady state CSTR design equations
  - In all three cases the outlet temperature and outlet molar flow rates make sense physically
  - Known as multiplicity of steady states

$$\dot{n}^0_{solvent}\hat{C}_{p,solvent}\left(T-T^0\right)=-k_0\exp\left\{\frac{-E}{RT}\right\}n_A\Delta H$$

CSTR Steady States



- Suppose the system was perturbed slightly away from a given steady state, would it tend naturally to return to that steady state
  - if so, it's a stable steady state (Points A & C)
  - if not, it's an unstable steady state. (Point B)
- Real systems won't operate naturally at an unstable steady state
- The start-up or most recent transient will determine which steady state is reached
  - Reactor design must include a safe and efficient start-up procedure that will bring the system to the desired steady state
- System is typically designed to operate at one of the steady states, not the other

Questions?

Activity 24.1

Consider an adiabatic, steady state CSTR with a fluid volume of 0.4 L. Suppose the liquid phase reaction A → Z takes place in the reactor. The feed to the reactor is at 330 K; it flows at 1 L min-1 and it contains 5 mol A L-1. The heat capacity of the solution is 1000 cal L-1 K-1, and it independent of both temperature and composition. The reaction is exothermic with a heat of -30,000 cal mol-1. The rate is first order in the concentration of A. The pre-exponential factor equals 4.8 x 1013 min-1 and the activation energy is 24,000 cal mol-1.

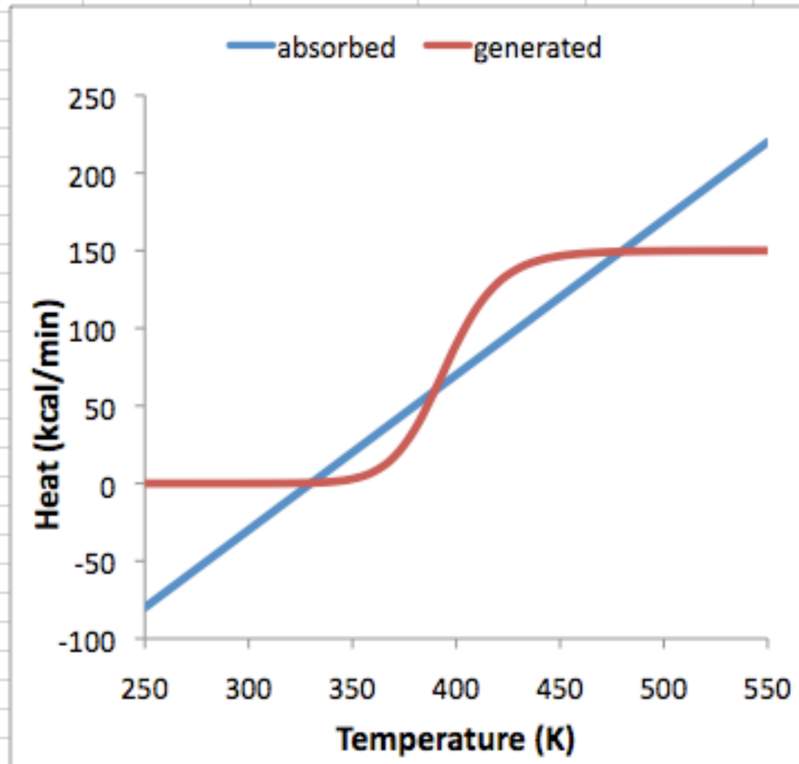
Write the steady-state mole balance on A and the energy balance for this reactor. Set up an Excel spreadsheet where each of the values given above are listed at the top. Then add columns for the outlet temperature, the outlet molar flow rate of A, the heat absorbed term and the heat generated term (see Unit 24). Fill in the temperature column with values from 250 to 550 K in steps of 10 K, and then enter formulae to fill in the other columns. Finally, on the same graph plot the heat absorbed versus T and the heat generated versus T. Call this your base case. Vary each parameter in the problem statement and determine how it affects the plot.

As you vary the parameters

- On a separate piece of paper write down whether varying a parameter changed the number of steady states and how
  - e. g. increasing the ? caused the number of steady states to increase

vfr =	1	L/min
T0 =	330	K
CA0 =	5	mol/L
cp =	1.00E+03	cal/L/K
V	0.4	L
dH	-30000	cal/mol
k0	4.8E+13	/min
E	24000	cal/mol

T	k	nA	absorbed	generated
250	4.9971E-08	4.9999999	-80	2.9983E-06
300	0.00015697	4.99968609	-30	0.00941739
310	0.00057525	4.99884977	-20	0.03450676
320	0.00194378	4.99611547	-10	0.11653597
330	0.00610087	4.98782797	0	0.36516094
340	0.01790262	4.96444934	10	1.06651979
350	0.04939988	4.9031147	20	2.90655914
360	0.12883852	4.75495162	30	7.35145131
370	0.31905226	4.43411432	40	16.9765705
380	0.75327016	3.84228773	50	34.7313682
390	1.70179377	2.97491992	60	60.7524023
400	3.69118053	2.01900105	70	89.4299685
410	7.70940387	1.2243614	80	113.269158
420	15.5469461	0.69263796	90	129.220861
430	30.3459556	0.38056436	100	138.583069
440	57.4584636	0.20847766	110	143.74567
450	105.751086	0.11547228	120	146.535832
460	189.538279	0.06509119	130	148.047264
470	331.379421	0.03743867	140	148.87684
480	566.036728	0.02198627	150	149.340412
490	945.960744	0.01317925	160	149.604623
500	1548.747	0.00805803	170	149.758259
510	2487.08983	0.00502091	180	149.849373
520	3921.84573	0.00318524	190	149.904443
530	6078.90597	0.00205545	200	149.938337
540	9270.66533	0.00134798	210	149.959561
550	13922.9561	0.00089764	220	149.973071



Results

$$\dot{n}^{0}_{solvent}\hat{C}_{p,solvent}\left(T-T^{0}\right)=-k_0\exp\left\{\frac{-E}{RT}\right\}n_A\Delta H$$

- Increasing the volumetric flow rate shifts the heat absorbed curve upward
- Increasing the inlet temperature shifts the heat absorbed curve downward
- Increasing the inlet concentration increases the size of the step in the heat generated curve
- Increasing the heat capacity decreases the size of the step in the heat generated curve
- Increasing the reaction volume shifts the step of the heat generated curve to lower temperature
- Increasing the heat of reaction (making it less negative) decreases the size of the step in the heat generated curve
- Increasing the pre-exponential factor shifts the step of the heat generated curve to lower temperature
- Increasing the activation energy shifts the step of the heat generated curve to higher temperature

Activity 24.2

- Choose a set of conditions from Activity 24.1 where the reactor displays three steady states
- Write the steady state mole balance and energy balance design equations for that CSTR
- Set up a MATLAB or other computer code to solve the design equations and use it to find all three steady states

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