MSE 120 – Materials Production

Instructor M.P. Sherburne

Midterm – Thursday Oct. 29, 2015

12:30-2:00 384 Hearst Mining Building

Name: ______________________________________

Name ________________________

SID __________________________

Problem	Score	Out of
1		/30
2		/20
3		/30
4		/20
Total		100

Equation Sheet:

$$C_m \approx \frac{10}{G} \qquad t_{ex,d} = \frac{100}{r}\ln\{\frac{rR}{100P}+1\} \qquad \frac{dP}{dt} = \frac{r}{100}P$$

$$H = \frac{FreeEnergyofFormation}{MolecularWeight} \qquad t_{ex,s} = \frac{R}{P} \qquad P = P_0 \exp\{\frac{r(t-t_0)}{100}\}$$

$$R_i = -\frac{1}{V}\frac{dN_i}{dt} = -\frac{dC_i}{dt} \qquad J = -D\frac{dC}{dx} \qquad C_{AS} = \frac{hk}{h+k}C_{AB} \qquad \frac{dR}{dt} = -\frac{M_Q}{\rho}\frac{hk}{h+k}C_{AB}$$

$$R_i = -\frac{1}{A}\frac{dN_i}{dt} \qquad J_A = h\left(C_{AB} - C_{AS}\right) \qquad r_Q = -\frac{\rho}{M_Q}\frac{dR}{dt} \qquad r_A = hC_{AB}\frac{R_O^2}{R^2}$$

$$k = A\exp\frac{-E_A}{RT} \qquad r_A = kC_A^{n_A} \qquad t_c = \frac{R_o}{c} \qquad R = R_o - \frac{M_Q k C_{AB}}{\rho}t$$

$$K = Exp(\frac{\Delta G}{RT})$$

Periodic Table – Atomic Masses

Key: 29 (Atomic number), Cu (Symbol), 63.54 (Atomic weight)

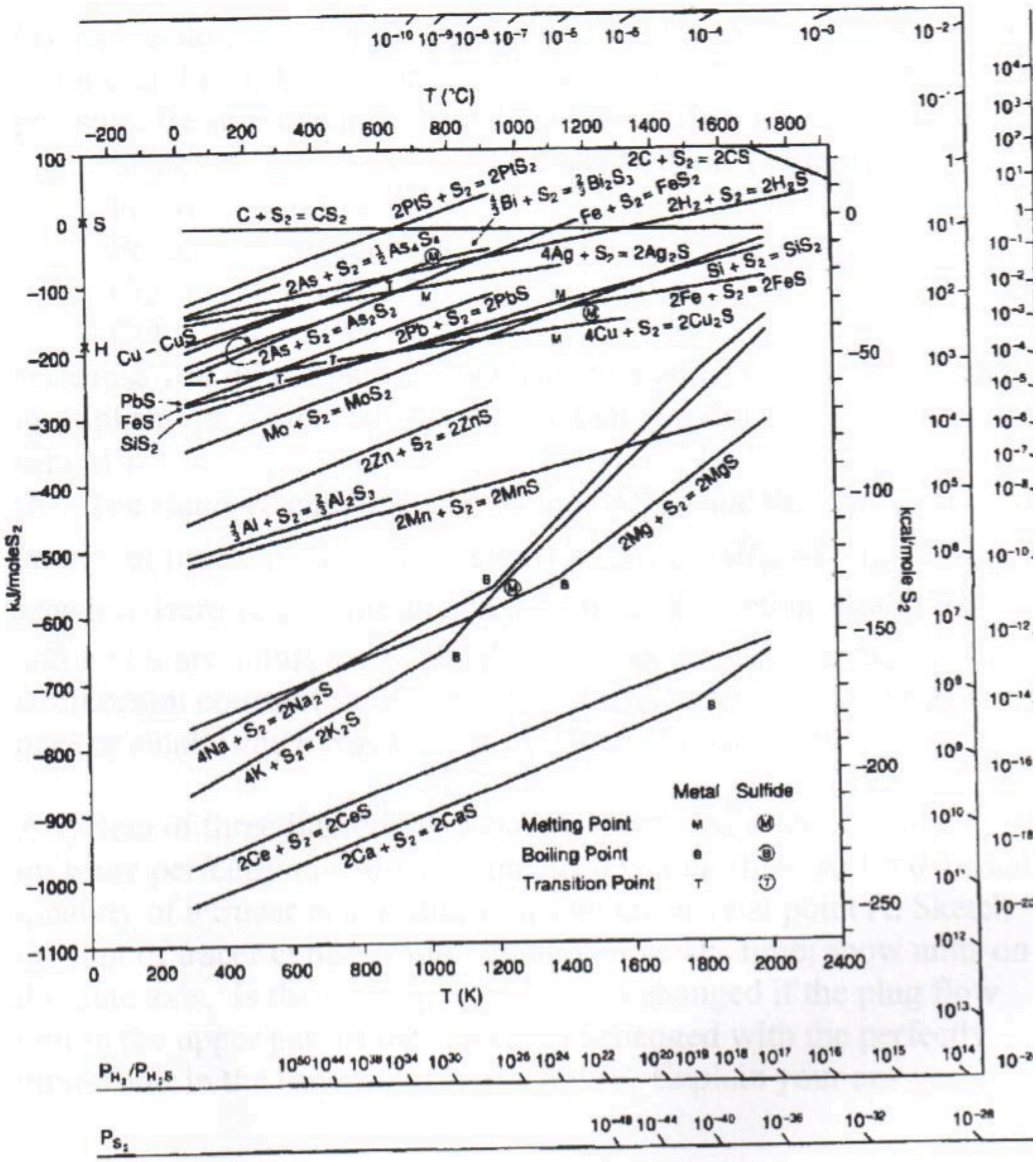
Metal

Nonmetal

Intermediate

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H 1.0080																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.87	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.69	29 Cu 63.54	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	Rare earth series	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.2	76 Os 190.23	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.19	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	Acti-nide series	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (281)								

Rare earth series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinide series	89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)


T (°C)
T (K)
kJ/moleS₂
kcal/mole S₂
C + S₂ = CS₂
2PtS + S₂ = 2PtS₂
2C + S₂ = 2CS
Fe + S₂ = FeS₂
2H₂ + S₂ = 2H₂S
2As + S₂ = ½ As₄S₄
4Ag + S₂ = 2Ag₂S
Si + S₂ = SiS₂
2Fe + S₂ = 2FeS
2As + S₂ = As₂S₂
2Pb + S₂ = 2PbS
4Cu + S₂ = 2Cu₂S
Cu - CuS
PbS
FeS
SiS₂
Mo + S₂ = MoS₂
2Zn + S₂ = 2ZnS
2Mn + S₂ = 2MnS
2Mg + S₂ = 2MgS
4Na + S₂ = 2Na₂S
4K + S₂ = 2K₂S
2Ce + S₂ = 2CeS
2Ca + S₂ = 2CaS
Metal Sulfide
Melting Point
Boiling Point
Transition Point
P_H₂/P_H₂S
P_S₂

You have finished your bachelors' degree, congratulations, and showing your intelligence once again you have decided to forgo graduate school and go to work in the real world. You have two companies, LexCorp and Wayne Industries, fighting for your services, because of your vast knowledge in materials processing gained from MSE 120. You have decided to take the position at Wayne Industries, because while Mr. Wayne is not overly friendly you do not get the feeling that he is a criminal, which you got from Lex Luthor of LexCorp. Also this gives you a chance to work with Lucius Fox a fantastic scientist/engineering.

1. *(20 pts.) General Materials Production*

   Prior to turning you lose on the problem they want you to solve Mr. Fox asked you some basic questions relevant to materials processing.

   (Circle the correct answer. If it is not clear what you are circling you are wrong!)

   a. (2 pts) The Bronze Age followed the Iron Age because early metallurgist exhausted the supply of iron.
      i. True
      ii. False

   b. (2 pts) Almost all of our inorganic materials are derived from the Chalcosphere.
      i. True
      ii. False

   c. (2 pts) An element, for which the line in the Ellingham diagram for oxides is lower than the line for a second element, will readily reduce the oxide of the second element.
      i. True
      ii. False

d. (2 pts) In carrying out an enthalpy balance the heat generated (or consumed) by any chemical reactions should be that at the reference temperature, rather than the actual temperature at which the reaction proceed.

   i. True
   ii. False

e. (2 pts) When a system undergoes a change, more work is done by the system if the change is carried out reversibly, than when the change is carried out irreversibly.

   i. True
   ii. False

f. (5pts.) In the production of metals the most important reducing agent (in terms of tons used per year by the industrialized nations) is

   i. Hydrogen
   ii. Carbon
   iii. Nutrasweet
   iv. Oxygen
   v. Sulfuric acid

g. (5pts.) The statement “At equilibrium a system is at the minimum Gibbs’ free energy.” Is

i. Always true
ii. Always false
iii. True provided the minimum is with respect to other states at the same pressure
iv. True provided the minimum is with respect to other states at the same temperature and pressure
v. None of the above

h. (5pts.) Consider a component of a solution that can also exist in the gas above the solution. At equilibrium one variable is the same in the solution and the gas. That variable is

i. The activity of the component
ii. The concentration of the component
iii. The standard state of the component
iv. The activity coefficient of the component
v. The chemical potential of the component

i. (5pts.) The rate equation for a reaction, A + B = C + D is found to be $\Re = k_f C_A^2 - k_b C_C$. The reaction is probably

i. Homogeneous and reversible
ii. Heterogeneous and irreversible
iii. First order in A
iv. Obeying Lanmuir-Hinshelwood kinetics
v. Heterogeneous and reversible

2. *(20 pts.) Resources*

Having impressed Lucius Fox with your ability to answer fundamental questions about materials processing. He tells you what project you are going to be working on. About 30 years ago a swarm of meteors hit Kansas and brought with it a mineral/element, which was not known to the earth prior to the meteor strikes. The new element is called kryptonite, and has been very difficult to purify. Mr. Fox is interested in how you would start processing the meteorites and how much you think the refined element would be worth.

The average meteorite piece that made it to the surface of the earth is 1 meter in diameter. With some cleaver characterization it has been determined that the average size of the kryptonite crystals is 1cm.

i. (5 pts) What would be the first step in processing the meteorite to extract the mineral of interest? (Short answer)

Physical Processing: Crushing, with jaw crusher
Grinding, with ball mill.

ii. (5 pts) When processing by pyrometallurgy what would be the desired average size of the rock to be processed? (Short answer)

The desired size of the rock should be of the order of the average kryptonite crystal size. Thus ~1cm.

iii. (5 pts) It has been estimated that the total weight of the meteorite is 3,000,000 kg and that the kryptonite continued in the meteorites is 250kg, what is the grade? (Calculation)

*250kg/3000000kg * 100 = 0.00833%*

iv. (5 pts) Knowing the ore grade can you give an estimate of the cost of the kryptonite? (Calculation)

C = 10/grade = $1,200/kg

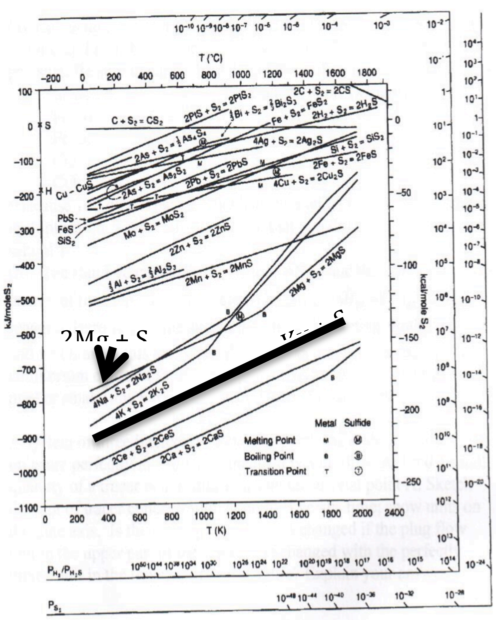
3. *(30 pts.)*
A chemical analysis of the kryptonite-containing mineral shows that it is bonded to sulfur as a sulfide (KyS, Ky = kryptonite). Your job is to figure out how to extract kryptonite from the minerals in the meteorite.

a) (5 pts) Knowing that the kryptonite is in the form of a sulfide and that kryptonite has a high affinity for oxygen what type of processing would you do? (Short answer)

Roasting. ***(3/2)***

Heat up KyS in a crucible with oxygen or air. KyO will form via the equation:

$KyS(s) + 2O_2(g) = KyO_2(s) + SO_2\ (g)$ ***(2/3)***



b) (5 pts) One of your coworkers has suggested that it should be possible to reduce KyS to Ky in a crucible of MgS. (short answer reference the Ellingham diagram below)

Not possible. ***(2)***
Looking at the Ellingham diagram, Ky+S = KyS is always lower than $2Mg + S_2 = 2MgS$. ***(2)***
Therefore, at any temperature and pressure, KyS is thermodynamically more stable than MgS. Thus, for any reduction reaction, MgS will be more favorably reduced to Mg before KyS goes to Ky. Which will render the reduction of KyS impossible *(1)*.

c) (5 pts) Knowing that the KyS will react with oxygen and produce an oxide and sulfur dioxide, write the balanced chemical reaction.

KyS (s) + $2O_2$ (g) = KyO_2 + SO_2 (g) ***(5)***

KyS (s) + $3/2O_2$ (g) = KyO_2 + SO_2 (g) ***(5)***

d) (5 pts) For your equation in part (c) writes the equilibrium constant assuming that the solids are not pure.

$$K = \frac{Products}{Reactants} = \frac{a_{KyO_2} a_{SO_2}}{a_{KyS} a_{O_2}} = \frac{\gamma_{KyO_2} \chi_{KyO_2} P_{SO_2}}{\gamma_{KyS} \chi_{KyS} P_{O_2}} \qquad \textbf{(5)}$$

$$= \frac{a_{KyO_2} P_{SO_2}}{a_{KyS} P_{O_2}} \qquad \textbf{(5)}$$

(4) for just the activities.
(3) for correct general idea.

e) (5 pts) Assuming that the processing will occur at 1200K, the solids can be treated as pure and the oxygen partial pressure of .25 atm, the R = 8.31447 J mol^{-1} K^{-1}. What is the partial pressure of SO_2?

$$K = Exp\left(\frac{\Delta G}{RT}\right) = \frac{P_{SO_2}}{P_{O_2}}$$

$$\Delta G = -700kJ/mol$$

Plug in the numbers and you can get:

$$P_{SO_2} = 1.91 * 10^{29} atm$$

f) (5 pts) Would this reaction go to completion? Justify your answer in terms of the equilibrium constant.

Yes it will. ***(2)***
The value of the equilibrium constant is many times above 10. ***(3)***

4. *(20 pts.)*

a) (10 pts) You have converted the sulfide to an oxide. Through traditional pyrometallurgy processes you find that the oxide KyO_2 is reduced to Ky_2O_3 when reacted with carbon monoxide at 1400K and atmospheric pressure. Calculate the standard heat (enthalpy) of reaction for this process.

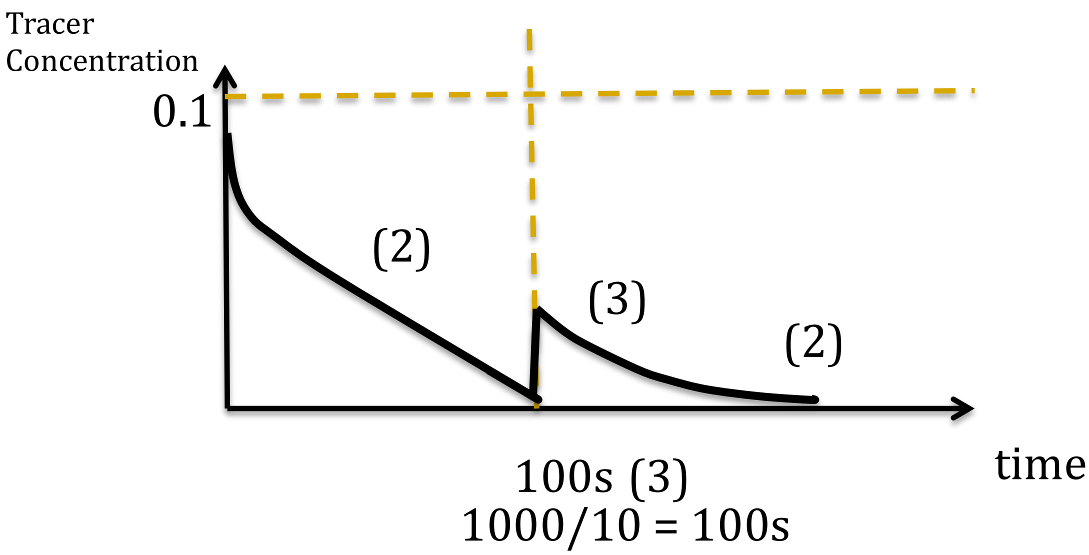
   a. The standard enthalpies at 1400K are:
      i. KyO_2 -802 (kJ/mol)
      ii. Ky_2O_3 -1086 (kJ/mol)
      iii. CO -112 (kJ/mol)
      iv. CO_2 -394 (kJ/mol)

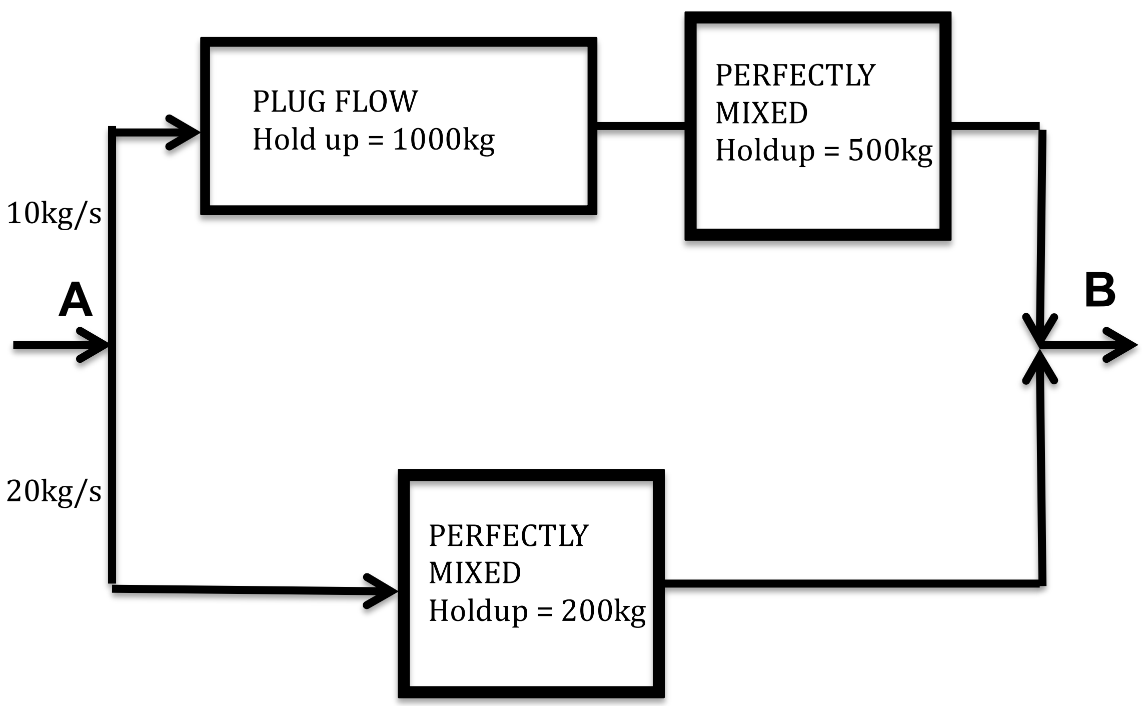
$2KyO_2 + CO = Ky_2O_3 + CO_2$ ***(5)***

$\Delta H_{Rxn} = \Delta H_{Ky_2O_3} + \Delta H_{CO_2} - 2\Delta H_{KyO_2} - \Delta H_{CO}$ ***(3)***

$\Delta H_{Rxn} = 236 \text{ kJ/mol}$ ***(2)***

b) (10 pts) Now you are going to attempt to process this compound by interconnecting three unit operations, as shown below. Two are perfectly mixed, while the third is plug flow. Prior to placing the kryptonite mineral in the system you run a test with a tracer. At t = 0 a small amount of tracer is introduced instantaneously at point A. Sketch the plot of tracer concentration at point B versus time. Be sure to label your plot.





Scratch Paper