CHAPTER 6

ENERGY BALANCES THAT INCLUDE THE EFFECTS OF CHEMICAL REACTION

1 Analysis of the Degrees of Freedom to Include
  the Energy Balance with Reaction
2 Applications of Energy Balances in Processes
  that Include Reactions

EXAMPLE 26.1   Analysis of the Degrees of Freedom for a Combustion Process

Methane is burned with 5% excess air in a furnace. Figure E26.1 shows the stream compositions and those variables whose values are specified. The process occurs with each stream at 1 atm. Determine if the number of degrees of freedom for the process is zero.
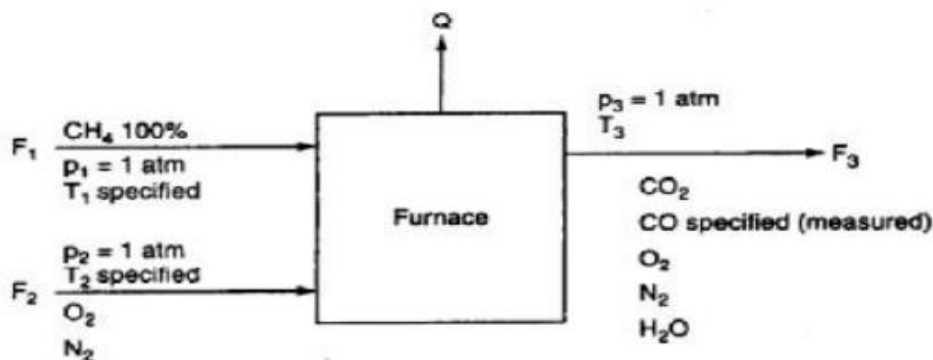

Figure E26.1

Solution

You should make a table to help in the count of the variables and equations. The energy balance is assumed to reduce to $Q = \Delta H$; replace ΔH as a variable with p and T.

Number of variables in the process (ignoring those with zero value):

Species in F_1	1	
F_2	2	
F_3	5	8
Total stream flows		3
Stream temperatures		3
Stream pressures		3
Q		1
Extent of reaction (2 reactions)		2
Total		20

Number of equations:

Independent species material balances	6
Sum of species in each of the 2 streams ($\Sigma n_i^j = F_j$)	2
Energy balance	1
Specification of the value of a variable	
Total stream flows (F_1, the basis, and F_2 comes from 5% excess air)	2
Species values (CO)	1
Pressures ($p_1 = p_2 = p_3 = 1$ atm)	3
Temperatures (T_1 and T_2)	2
O_2 to N_2 ratio specified in F_2 (an implicit specification)	1
Complete reaction (no CH_4 in exit stream exists) hence the extent of reaction is implied for both reactions (to CO and CO_2)	2
Thus, the degrees of freedom are zero	20

If you include the Ar in the air that enters with the O_2 and N_2 so that Ar appears in the exit gas from the furnace, how will the degree-of-freedom analysis be affected? Hints: (a) Does Ar react? (b) Is the Ar entering specified? How would the analysis above change if you used element instead of species material balances?

2 Applications of Energy Balances in Processes that Include Reactions

- With the effects of chemical reaction merged with the sensible heats

$$Q = \Delta H = [H(T) - H(25°C)]_{outputs} - [H(T) - H(25°C)]_{inputs} \qquad (26.1a)$$
$$= \Delta H_{outputs} - \Delta H_{inputs}$$

- With the effects of chemical reaction lumped in the heat of reaction

$$Q = [H(T) - H(25°C)]_{outputs}^{sensible + phase\ change} - [H(T) - H(25°C)]_{inputs}^{sensible + phase\ change}$$
$$+ \Delta H_{rxn} \qquad (26.1b)$$

We will use Equation (26.1a) in the examples below.
Here are some typical problems frequently posed for open systems:

1. What is the temperature of one stream given data for the other streams?
2. How much heat has to be added to or removed from the process?
3. What is the temperature of the reaction?
4. How much material must be added or removed from the process to give a specified value of heat transfer?

A topic related to question #1 above pertains to a special term called the **adiabatic reaction (theoretical flame, combustion) temperature,** which is defined as the temperature obtained inside the process when

1. the reaction is carried out under adiabatic conditions, that is, there is no heat interchange between the vessel in which the reaction is taking place and the surroundings;
2. no other effects occur, such as electrical effects, work, ionization, free radical formation, and so on; and
3. the limiting reactant reacts completely.

For an unsteady-state *closed system* with ΔKE and $\Delta PE = 0$ inside the system and $W = 0$, the energy balance becomes

$$Q = \Delta U = U_{final} - U_{initial} \tag{26.2}$$

If you do not have values for $\Delta \hat{U}$, you have to calculate ΔU from $\Delta H - \Delta(pV)$ in which the heats of formation are meshed with the sensible heats and phase changes

$$Q = [H(T) - H(25°C)]_{final} - [H(T) - H(25°C)]_{initial}$$
$$-[(pV)_{final} - (pV)_{initial}] \tag{26.3}$$

The contribution of $\Delta(pV)$ is frequently negligible. For a constant volume process, $\Delta(pV) = V\Delta p$, and for a constant pressure but expandable closed system $\Delta(pV) = p\Delta V$. For the special case of an ideal gas, $\Delta(pV) = \Delta(nRT) = R\Delta(nT)$.

EXAMPLE 26.2   Calculation of an Adiabatic Reaction (Flame) Temperature

Calculate the theoretical flame temperature for CO gas burned at constant pressure with 100% excess air, when the reactants enter at 100°C and one atm.

Solution

The solution presentation will be compressed to save space. The system is shown in Figure E26.2. We will use data from the Appendix and the CD in the back of this book. The process is a steady-state flow system. Ignore any equilibrium effects.

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$
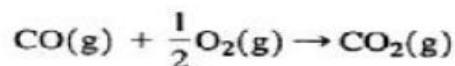
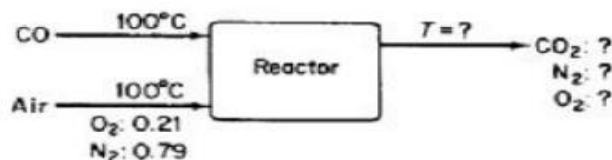Basis: 1 g mol of CO(g); ref. Temp. 25°C and 1 atm

Figure E26.2

The reaction is always assumed to occur with the limiting reactant completely reacting. The excess air is a nonreacting component, but requires sensible heat to raise its temperature to the adiabatic reaction temperature.

the solution of the material balances is:

Entering compounds		Exit compounds	
Component	g mol	Component	g mol
CO(g)	1.00	CO_2(g)	1.00
O_2(req. + xs)		O_2(g)	0.50
0.50 + 0.50	1.00	N_2(g)	3.76
N_2	3.76		
(Air = 4.76)			

Select the reference state to be 25°C and 1 atm. In the first approach to the solution of the problem, the "sensible heat" (enthalpy) values have been taken from the table of the enthalpy values for the combustion gases in Appendix D. They could not be calculated using the physical property software on the accompanying CD as the states at 1000 K are out of range. The energy balance (with $Q = 0$) reduces to $\Delta H = 0$. Here is the data needed for the energy balance.

Component	g mol	T(K)	$\Delta \hat{H}$(J/g mol)	$\Delta \hat{H}_f^o$(J/g mol)	ΔH (J)
Inputs					
CO	1.00	373	(2917–728)	−110,520	−108,331
O_2	1.0	373	(2953–732)	0	2,221
N_2	3.76	373	(2914–728)	0	8,219
		Total			−97,891
Outputs					
Assume T = 2000K:					
CO_2	1.00	2000	(92,466–912)	−393,510	−301,956
O_2	0.50	2000	(59,914–732)	0	29,591
N_2	3.76	2000	(56,902–728)	0	211.214
		Total			−61,151

$$\Delta H = \Delta H_{outputs} - \Delta H_{inputs} = (-61,151) - (-97,891) = 36,740 > 0$$

Assume T = 1750K:

CO_2	1.00	1750	(77,455–912)	−393,510	−316,977
O_2	0.50	1750	(50,555–732)	0	24,912
N_2	3.76	1750	(47,940–728)	0	177,517
		Total			−114,548

$$\Delta H = (-114,548) - (-97,891) = -16,657 < 0$$

Now that $\Delta H = 0$ is bracketed, we can carry out a linear interpolation to find the theoretical flame temperature (TFT):

$$TFT = 1750 + \frac{0 - (-16,657)}{36,740 - (-16,657)}(250) = 1750 + 78 = 1828K \; (1555°C)$$

EXAMPLE 26.3   Application of the General Energy Balance in a Process in which More Than One Reaction Occurs

Limestone ($CaCO_3$) is converted to calcium oxide (CaO) in a continuous vertical kiln as illustrated in Figure E26.3a. The energy to decompose the limestone is supplied by the combustion of natural gas (CH_4) in direct contact with the limestone using 50% excess air. The $CaCO_3$ enters the process at 25°C and the CaO exits at 900°C. The CH_4 enters at 25°C and the product gases exit at 500°C. Calculate the number of pounds of $CaCO_3$ that can be processed per 1000 ft³ of CH_4 measured at standard conditions. To simplify the calculations, assume that the heat capacities of $CaCO_3$ (56.0 Btu/ (lb mol) (°F)) and CaO (26.7 Btu/(lb mol)(°F)) are constant.

Figure E26.3a shows a vertical line kiln comprised of a steel cylinder lined with fire brick approximately 80 ft high and 10 ft in diameter. Fuel is supplied at A, air at B, and limestone ($CaCO_3$) at E. Combustion products and CO_2 exit at D.
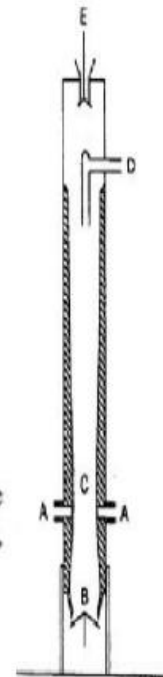

Figure E26.3a

Solution

In this problem the material and energy balances are coupled and must be solved simultaneously. The process is open and steady state.

Let us start with a basis of 1 g mol CH_4 for convenience. Many other bases could be selected.

The heat capacities of $CaCO_3$ and CaO, respectively, in kJ/g mole are:

$CaCO_3$	0.130 kJ/g mol	MW = 100.09
CaO	0.062 kJ/g mol	MW = 56.08

The reactions are

(a) $CaCO_3$ (s, 25°C) → CaO (s, 900°C) + CO_2 (g, 500°C)
(b) CH_4 (g, 25°C) + $2O_2$ (g, 25°C) → CO_2 (g, 500°C) + $2H_2O$ (g, 500°C)

The moles of O_2 and N_2 entering are

1 mol CH_4 requires:	2 g mol O_2
50% excess:	1
Total O_2	3
Entering N_2:	3 (0.79/0.21) = 11.29 g mol

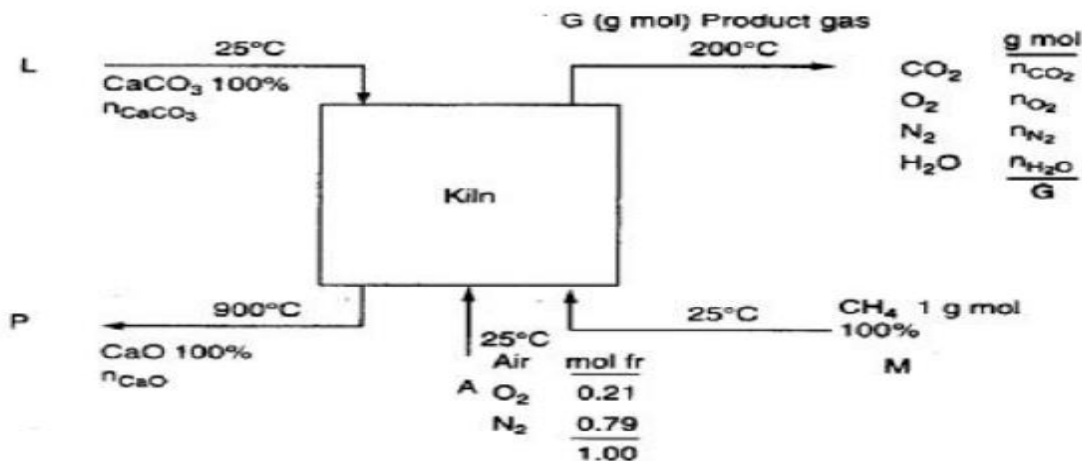You can use Figure E26.3b as a guide for the material and energy balances.

Figure E26.3b

If we can assume $Q = 0$ approximately, the energy balance reduces to $\Delta H = 0$.

The element material balances reduce to in = out.

Balance	In		Out	
C:	$1 + L$	$=$	$n^G_{CO_2}$	(1)
2N:	11.29	$=$	$n^G_{N_2}$	(2)
H:	4 (1)	$=$	$2n^G_{H_2O}$ hence $n^G_{H_2O} = 2$	(3)
O:	$3L + 2(3)$	$=$	$2n^G_{CO_2} + 2n^G_{O_2} + n^G_{H_2O} + P$	(4)
Ca:	L	$=$	P	(5)

      To write an energy balance you need to get data on all of the heats of formation of the respective species and the enthalpies for the "sensible" heats.

      We will combine the heats of formation with sensible heat data from the software on the CD that accompanies this book. The values for the heats of formation of the solid species are from Appendix F.

Species	g mol	$T(°C)$	$\Delta \hat{H}^o_f$(kJ/g mol)	Sensible heats ΔH^o_f(kJ/g mol)	Stream ΔH(kJ)
Out					
$CO_2(g)$	$n^G_{CO_2}$	500	−393.250	21.425	$−371.825 n^G_{CO_2}$
$O_2(g)$	1	500	0	15.034	15.034
$N_2(g)$	11.29	500	0	14.241	160.781
$H_2O(g)$	2	500	−241.835	17.010	−449.650
$CaO(2)$	P	900	−635.6	(0.062)(100−25)	$−581.35P$
In					
$CH_4(g)$	1	25	−49.963	0	−49.963
$CaCO_3(s)$	L	25	−1206.9	0	$−1206.9L$
$O_2(g)$	3	25	0	0	0
$N_2(g)$	11.29	25	0	0	0

Thus, the energy balance is with $(P = L)$

$$-371.825n^G_{CO_2} + 15.304 + 160.781 - 449.650 - 581.350L$$
$$= -49.963 - 1206.9L \qquad (6)$$

Solve Equation (1) and (6) simultaneously to get

$$L = 2.56 \text{ g mol}$$

On the basis of 1 g mol CH_4

$$\frac{2.56 \text{ g mol } CaCO_3}{1 \text{ g mol } CH_4} \bigg| \frac{100.09 \text{ g } CaCO_3}{1 \text{ g mol } CaCO_3} = \frac{256 \text{ g } CaCO_3}{1 \text{ g mol } CH_4}$$

To get the ratio asked for (assuming CH_4 is an ideal gas—a good assumption)

$$\frac{1000 \text{ ft}^3 CH_4}{} \bigg| \frac{1 \text{ lb mol}}{359.05 \text{ ft}^3} \bigg| \frac{256 \text{ lb } CaCO_3}{1 \text{ lb mol } CH_4} = \frac{713 \text{ lb } CaCO_3}{1000 \text{ ft}^3 CH_4 \text{ at SC}}$$

EXAMPLE 26.4   Application of the Energy Balance to a Process Composed of Multiple Units

Figure E26.4a shows a process in which CO is burned with 80% of the theoretical air in Reactor 1. The combustion gases are used to generate stream, and also to transfer heat to the reactants in Reactor 2. A portion of the combustion gases that are used to heat the set of tubes in Reactor 2 are recycled. SO_2 is oxidized in Reactor 2. You are asked to calculate the lb mol of CO burned per hour in Reactor 1. Note: The gases involved in the SO_2 oxidation do not come in direct contact with the combustion gas used to heat the SO_2 reactants and products.

Data for Reactor 2 pertinent to the SO_2 oxidation is

Reactants	mol fr.	T °F
SO_2	0.667	77
O_2	0.333	77
	1.00	

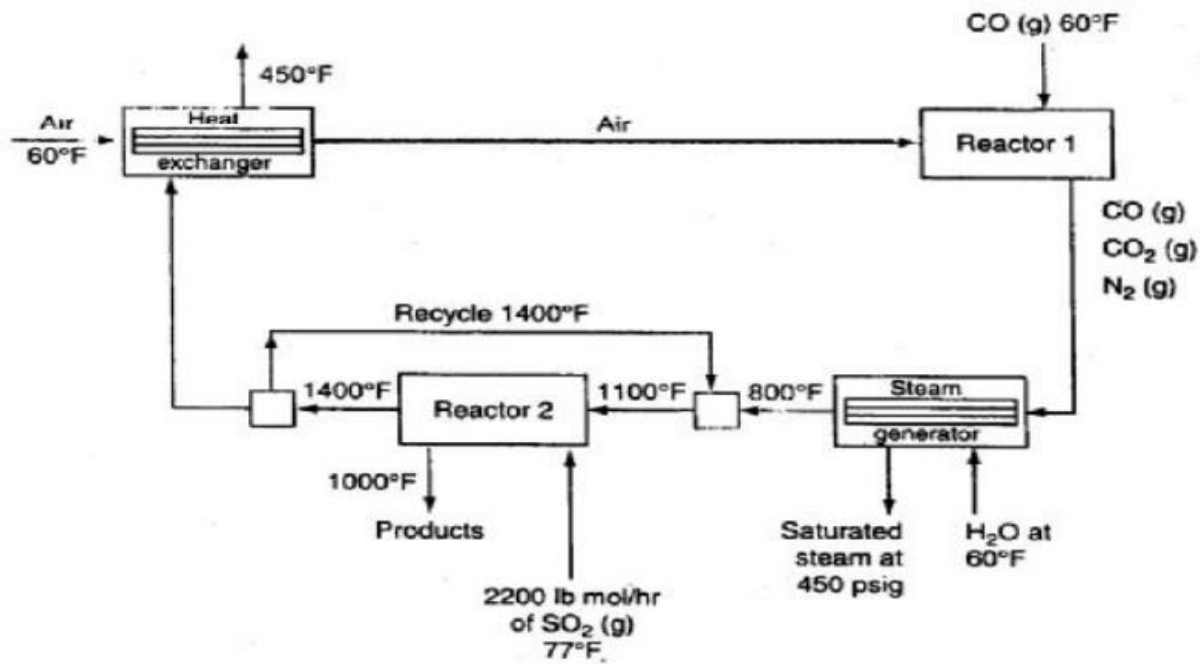| Products	mol fr.	T °F
SO_3	0.586	1000
SO_2	0.276	1000
O_2	0.138	1000
	1.000	

Figure E26.4a

Solution

sumptions:

1. The process is a continuous flow process, hence $\Delta E = 0$
2. The pressure everywhere is 1 atm.
3. No heat loss occurs ($Q = 0$ in the energy balances)
4. $\Delta KE = \Delta PE = W = 0$

Basis: 1 g mol CO entering Reactor 1

A figure helps in the analysis—examine Figure E26.4b. The system is Reactor 2 excluding the recycle stream.
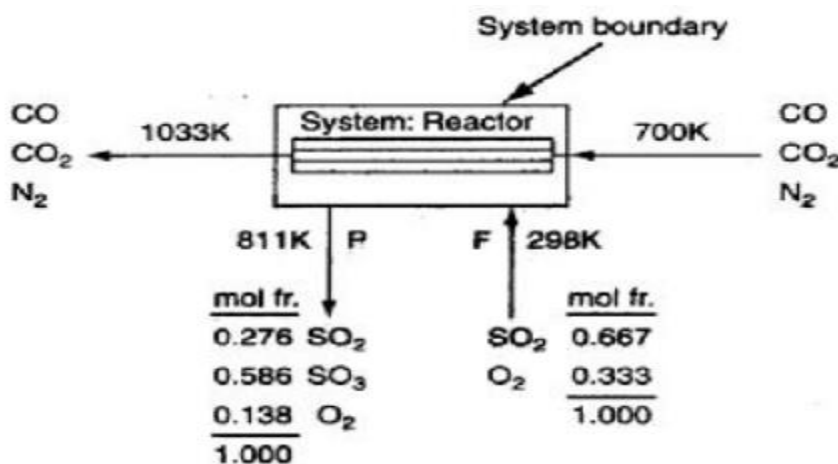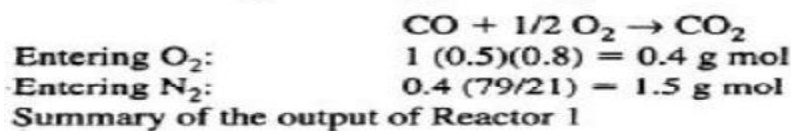

Figure E26.4b

Basis: 1 g mol CO(g) entering Reactor 1

$$CO + 1/2\ O_2 \rightarrow CO_2$$

Entering O_2:   1 (0.5)(0.8) = 0.4 g mol
Entering N_2:   0.4 (79/21) = 1.5 g mol
Summary of the output of Reactor 1

Component	g mol	mol fr.
CO	1(1 −0.8) = 0.2	0.32
CO_2	1(0.8) = 0.8	0.08
N_2	= 1.5	0.60
Total	2.5	1.00

SO_2: $P(0.276) - F(0.667) = -1(\xi)$ (a)

SO_3: $P(0.586) - F(0) = 1\ (\xi)$ (b)

O_2: $P(0.138) - F(0.333) = -0.5(\xi)$ (c)

Because Equations (a) to (c) are a set of homogeneous equations $f(x) = 0$, that is, when each equation is rearranged and set equal zero, every term is associated with a variable. As pointed out in Appendix L1, no nontrivial solution exists. Try to solve Equations (a)–(c), and you will see this condition is true. Thus, one more equation is needed. Use an energy balance.

For you to make an energy balance you have to get information about the heats of formation and the sensible heats. The data used below have been taken from the CD in the back of this book. With the assumptions made, the energy balance reduces to $\Delta H = 0$.

Data and Calculations for the Energy Balance

Comp	g mol	T(K)	$\Delta \hat{H}_f^\circ$ (kJ/g mol)	$\Delta \hat{H}_{sensible}$ (kJ/g mol)	ΔH (kJ)
Out					
CO(g)	0.2	1033	−109.054	35.332	−14.744
CO_2(g)	0.8	1033	−393.250	35.178	−286.458
N_2(g)	1.5	1033	0	22.540	33.810
SO_2(g)	$n_{SO_2}^P$	811	−296.855	20.845	$-276.010 n_{SO_2}^P$
SO_3(g)	$n_{SO_3}^P$	811	−395.263	34.302	$-360.961 n_{SO_3}^P$
O_2(g)	$n_{O_2}^P$	811	0	16.313	$16.313 n_{O_2}^P$
In					
CO(g)	0.2	700	−109.054	17.177	−18.375
CO_2(g)	0.8	700	−393.250	17.753	−300.398
N_2(g)	1.5	700	0	11.981	17.972
SO_2(g)	$n_{SO_2}^F$	298	−296.855	0	$-296.855 n_{SO_2}^F$
O_2(g)	$n_{O_2}^F$	298	0	0	0

The energy balance is

$$-276.010n_{SO_2}^P - 360.961n_{SO_3}^P + 296.855n_{SO_2}^F + 16.313n_{O_2}^P = -33.41n_{SO_2}^F \quad (d)$$

Substitute for the variables in Equation (d) the following to get Equation (d) in terms of F and P:

$$n_{SO_2}^P = P(0.276) \qquad n_{O_2}^P = P(0.138)$$
$$n_{SO_3}^P = P(0.586) \qquad n_{SO_2}^F = F(0.667)$$

Solve Equation (d) in terms of F and P together with Equations (a) and (b) (using Polymath) to get (the n_i are in g mol)

$$n_{SO_2}^P = 0.312 \qquad n_{SO_2}^F = 0.974$$
$$n_{SO_3}^P = 0.662 \qquad n_{O_2}^F = 0.486$$
$$n_{O_2}^P = 0.156$$
$$P = 1.13 \qquad \xi = 0.66$$
$$F = 1.46$$

Step 10

Check the solution using an oxygen balance

$$O: \quad 2n_{SO_2}^P + 3n_{SO_3}^P + 2n_{O_2}^P - 2n_{O_2}^F - 2n_{SO_2}^F = 0$$
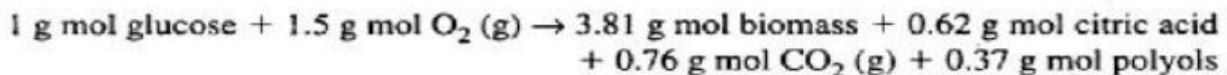$$2(0.312) + 3(0.662) + 2(0.156) - 2(0.486) - 2(0.974) = 0$$

Finally. you need to calculate the lb mol of CO/hr that flow into Reactor 1. Because no loss of combustion gases occurs up to and through Reactor 2, you know (on the basis of 1 g mol CO entering Reactor 1) that

$$\frac{1 \text{ lb mol CO}}{0.974 \text{ lb mol } SO_2} \left| \frac{2200 \text{ lb mol } SO_2}{hr} \right. = 2259 \frac{\text{lb mol CO}}{hr}$$
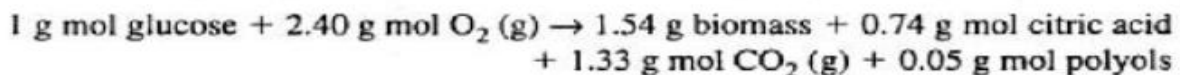
EXAMPLE 26.5   Production of Citric Acid by a Fungus

Citric acid is a well known compound that occurs in living cells for both plants and animals. The citric acid cycle is a series of chemical reactions occurring in living cells that is essential for the oxidation of glucose, a major source of energy for the cells. The reaction scheme is far too complicated to show here, but from a macroscopic (overall) viewpoint, for the commercial production of citric acid in a batch process, three different phases occur for which the stoichiometries are slightly different:

Early idophase (occurs between 80 and 120 hours), initial reaction

1 g mol glucose + 1.5 g mol O_2 (g) → 3.81 g mol biomass + 0.62 g mol citric acid
$$+ 0.76 \text{ g mol } CO_2 \text{ (g)} + 0.37 \text{ g mol polyols}$$

Medium idophase (occurs between 120 and 180 hours), additional glucose consumed

1 g mol glucose + 2.40 g mol O_2 (g) → 1.54 g biomass + 0.74 g mol citric acid
$$+ 1.33 \text{ g mol } CO_2 \text{ (g)} + 0.05 \text{ g mol polyols}$$

Late idophase (occurs between 180 and 220 hours), additional glucose consumed

1 g mol glucose + 3.91 g mol O_2 (g) + 0.42 g mol polyols → 0.86 g mol citric acid
$$+ 2.41 \text{ g mol } CO_2$$
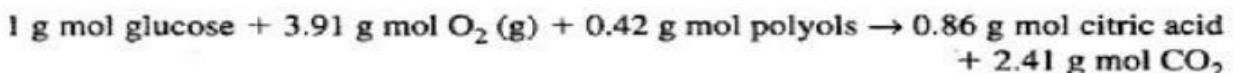
In an aerobic (in the presence of air) batch process, a 30% glucose solution at 25°C is introduced into a fermentor. Citric acid is to be produced by using the fungus *Aspergillus niger*. Stochiometric sterile air is mixed with the culture solution by a 100 hp aerator. Only 60% overall of the glucose supplied is expected to be converted to citric acid. The early phase is run at 32°C, the middle phase at 35°C, and the late phase at 25°C.

Based on the given data, how much heat has to be added or removed from the fermentor during the production of a batch of 10,000 kg of citric acid? Ignore any slight effects of solution on the value of the heat of formation.

<center>Data</center>

	MW	$\Delta \hat{H}^{\circ}_f$ (kJ/g mol)
d, α glucose ($C_6H_{12}O_6$)	180.16	−1266
Citric acid ($C_6H_8O_7$)	192.12	−1544.8
Dry cells (biomass)	28.6	−91.4

Solution

Let citric acid be denoted by CA and the biomass by BM. You can make a material balance for the overall process for which the total net reaction in g mol is

$$3 \text{ glucose} + 7.8 \text{ } O_2 \rightarrow 5.35 \text{ BM} + 2.22 \text{ CA} + 4.50 \text{ } CO_2$$
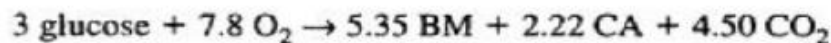
Material balance

<center>Basis: 10,000 kg CA produced</center>

$$\frac{10,000 \text{ kg CA}}{} \left| \frac{1 \text{ kg mol CA}}{192.12 \text{ kg CA}} \right. = 52.05 \text{ kg mol CA produced}$$

$$\frac{52.05 \text{ kg mol CA}}{} \left| \frac{3 \text{ kg mol glucose}}{2.22 \text{ kg mol CA}} \right| \frac{1.00 \text{ kg mol glucose introduced}}{0.60 \text{ kg mol glucose consumed}}$$

$$\times \frac{180.16 \text{ kg glucose}}{1 \text{ kg mol glucose}} \left| \frac{1.00 \text{ kg soln}}{0.30 \text{ kg glucose}} \right.$$

<center>= 70,400 kg of 30% solution introduced</center>

The water serves a a culture medium and does not enter the overall stoichiometry.

Summary of the material balances:

Component	Initial (kg mol)	Final (kg mol)
Glucose (70,400)(0.3)/180.16 =	117.32	46.93
BM (52.05) (5.35/2.22) =		125.44
CA		52.05
O_2 (accumulated) (117.32)(7.8/3) =	305.03	
$\overline{CO}_2$ (accumulated) (117.32)(4.5/3)(0.60)=		105.59

We will assume that the O_2 and N_2 drawn into the system and the CO_2 and N_2 leaving the system are deemed to be part of the initial state of the system and the final state, respectively, to maintain a closed system.

Energy balance

For the closed system

$$\Delta U = Q + W$$

because the changes in KE and PE inside the system are zero, and no flow occurs in or out of the system. The assumption about no flow is not correct, of course, because gas flows in at temperatures not specified, and flows out at various temperatures. However, if you were to calculate the energy associated with the gas flows, you would find it to be insignificant with respect to the work done on the system and the heat of reaction.

The work done is

$$W = \frac{100\ \text{hp}}{} \left| \frac{745.7\ \text{J}}{1\ (\text{hp})(\text{s})} \right| \frac{220\ \text{hr}}{} \left| \frac{3600\ \text{s}}{1\ \text{hr}} \right| \frac{1\ \text{kJ}}{1000\ \text{J}} = 5.906 \times 10^7\ \text{kJ}$$

Because we do not have value for U for this system, we will have to assume that

$$\Delta U = \Delta H - \Delta(pV) \cong \Delta H \text{ because } \Delta(pV) \text{ is negligible}$$

Then

$$Q = \Delta H - W$$

The next step is to calculate the enthalpy change. The reference temperature will be 25°C. The initial state is 25°C and the final state is also 25°C so that the sensible heats are zero. We will omit including the nitrogen in the energy balance because the nitrogen in equals the nitrogen out.

	Component	kg mol	$\Delta \hat{H}_f^\circ$(kJ/g mol)	$\Delta \hat{H}$ (kJ)
Initial	Glucose	117.32	-1266	$-148,530 \times 10^3$
	O_2	305.03	0	0
	Total			$-148,530 \times 10^3$
Final	Glucose	46.93	-1266	$-59,410 \times 10^3$
	BM	125.44	-91.4	$-11,470 \times 10^3$
	CA	52.05	-1544.8	$-80,410 \times 10^3$
	CO_2	105.59	-393.51	$-41,550 \times 10^3$
	Total			$-192,840 \times 10^3$

$$\Delta H = [(-192,840) - (-148,530)] \times 10^3 = -44,310 \times 10^3\ \text{kJ}$$

$$Q = -4.43 \times 10^7 - 5.91 \times 10^7 = -1.03 \times 10^8\ \text{kJ (heat removed)}$$

Notice This **Home Work**: *Basic Princeples and Calculation in Chemical Engineering*, 7th edition, **Problems of chapter 26, page 827 – 835**.