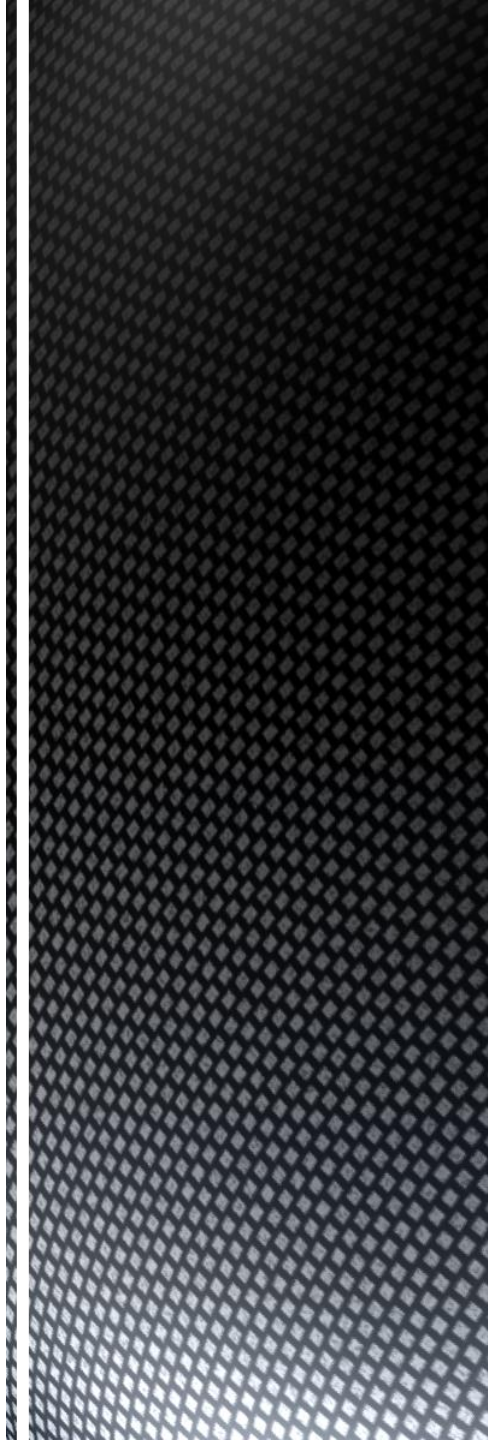


Materials and Energy Balance

The Heat Balance



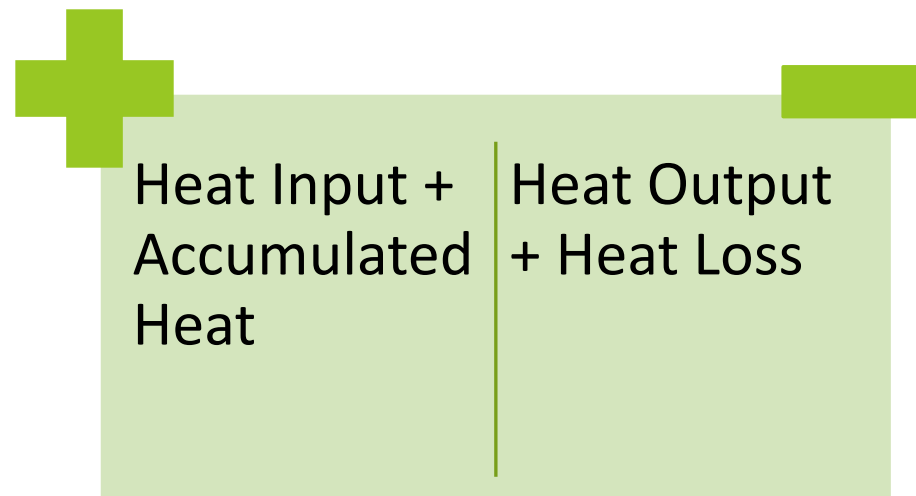
The heat balance shows the important sources of heat energy and their relative contribution to the total energy usage in a process

The heat balance like the material balance accounts for heat quantities in two categories, input and output, whose total must be identical

Careful study of the heat balance often discloses possible lines of improvement in the process, especially improvements leading to saving in fuel

Modifications for a process like change in compositions of input materials in fuel, in rate of treatment or in process temperature are often necessary

Understanding of the probable effects of such modifications on the heat balance helps the engineer in preparing for operating difficulties resulting from the changes



- Heat Input Items

- Sensible heats of input materials
- Heats evolved in exothermic reactions
- Heat supplied from outside of the system

- Heat Output Items

- Sensible heats of output materials
- Heats absorbed in endothermic reactions
- Heats absorbed in bringing input materials to reference temperature and state
- Heat loss to the surroundings

Heat input is equal to heat output in steady state processes

In autogeneous processes like roasting of zinc, the heat evolved in the metallurgical reactions themselves and the sensible heats in the input materials account for the heat input

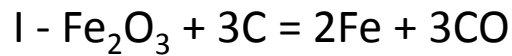
In non-autogeneous processes like ironmaking in reverberatory furnace, the heat is supplied wholly or in part by heat evolved from combustion of fuel, heat supplied electrically or by other means from outside the system

$$\text{Thermal efficiency} = \frac{\text{Useful heat output}(\text{total heat input} - \text{heat losses})}{\text{Total heat input}}$$

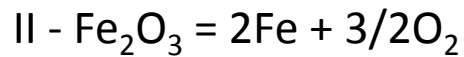
Procedure in Calculating a Heat Balance

1. Work out the complete stoichiometry of the reactions and materials balance
2. Denote the temperatures at which all materials enter and leave the system
3. Fix and specify the basis of the heat balance (quantity throughout the process), reference temperature and reference state for water and other substances
4. Calculate the sensible heat for each input and output material
5. Calculate heats of reaction for the quantities of all the chemical reactions
6. Calculate if present, heats required to bring input materials up to the reference states
7. Calculate if present, heat supplied electrically or by other means from the surroundings
8. List and add input and output items, finding heat loss by the difference

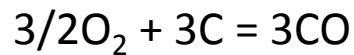
The question of which set of reactions should be used to account for the overall chemical change of the process is important



$$\Delta H_{298} = 117240 \text{ calories/mole Fe}_2\text{O}_3$$



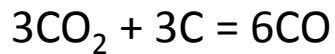
$$\Delta H_{298} = 196500 \text{ calories/mole Fe}_2\text{O}_3$$



$$\Delta H_{298} = -79260 \text{ calories/mole Fe}_2\text{O}_3$$



$$\Delta H_{298} = -6390 \text{ calories/mole Fe}_2\text{O}_3$$



$$\Delta H_{298} = 123630 \text{ calories/mole Fe}_2\text{O}_3$$

All three sets of reactions represent the same change in state, the net contribution to the heat balance is 117249 calories/mole Fe_2O_3

The heat output or heat consumption accompanying reaction I is represented as a single item in the heat output side of heat balance

The largest heat output and heat input are obtained by choosing set II, each heat input and output being 79260 calories larger than those of set I

For all three set, the heat loss to the surrounding that is calculated by the difference is the same

	Heat Input	Heat Output	ΔH for chemical change
Reaction set I	--	117240 cal	117240 cal
Reaction set II	79260 cal	196500 cal	117240 cal
Reaction set III	6390 cal	123630 cal	117240 cal

Thermodynamically, all three methods are equally correct

However the choice of set affects the outlook of the heat balance

Using the combination of reactions which gives the largest input and output totals gives greater emphasis on reaction heats compared to other items

The combination giving the largest input and output makes the heat loss appear in a smaller proportion of the total heat input so that a higher thermal efficiency than actual is obtained

$$\text{Thermal efficiency} = \frac{\text{Useful heat output}(\text{total heat input} - \text{heat losses})}{\text{Total heat input}}$$

The set of equations must represent real heat evolutions or absorptions in the process as much as possible

Example - Limestone of 84% CaCO₃, 8% MgCO₃, 8% H₂O is calcined in a rotary kiln. Gaseous fuel is combusted with stoichiometric air to supply the required heat. The limestone, fuel and air are supplied at 298 K, lime is discharged at 1173 K and gases leave at 473 K. Calculate the energy required to calcine 1000 kg of limestone.

Reactions:



Material balance gives calcined products and off-gases as

8.4 kg-moles CaO

0.952 kg-moles MgO

9.352 kg-moles CO₂

4.444 kg-moles H₂O

8.4 kg-moles CaO is produced by consuming $8.4 \times 42750 = 359100$ Kcal

0.952 kg-moles MgO is produced by consuming $0.952 \times 24250 = 23086$ Kcal

Total heats of decomposition of the two reactions = 382186 Kcal

The sensible heat in calcined products

$$\begin{aligned} \Delta H_{298}^{1173} &= 8.4 * \int_{298}^{1173} C_p(\text{CaO})dT + 0.952 * \int_{298}^{1173} C_p(\text{MgO})dT \\ &= 89547 + 9542 = 99089 \text{ Kcal} \end{aligned}$$

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The sensible heat in CO₂

$$\begin{aligned}\Delta H_{298}^{473} &= 9.352 * \int_{298}^{473} C_P(\text{CO}_2)dT \\ &= 16252 \text{ Kcal}\end{aligned}$$

The heat content in H₂O

$$\begin{aligned}\Delta H_{298}^{373} &= 4.444 * \int_{298}^{373} C_P(\text{H}_2\text{O}(l))dT + 4.444 * \Delta H_m + 4.444 * \int_{373}^{473} C_P(\text{H}_2\text{O}(v))dT \\ &= 6001 + 11158 + 3643 = 20802 \text{ Kcal}\end{aligned}$$

Total heat requirement to calcine 1000 kg of limestone

$$\Delta H = 518329 \text{ Kcal}$$

Example - Limestone is calcined in a rotary kiln. Gaseous fuel at 900 K is combusted with stoichiometric air to supply the required heat. The limestone and air are supplied at 298 K, lime is discharged at 1173 K and gases leave at 473 K. Calculate the amount of gaseous fuel required to obtain 10 kg-moles CaO

Reactions:



Rational Analysis wt%, v%							
	CaCO ₃	MgCO ₃	H ₂ O	CO ₂	O ₂	CO	N ₂
Limestone	84	8	8				
Fuel				7.2	1.6	16.6	74.6

The calorific value of the fuel or quantity of heat produced by combustion of 1 kg-mole of fuel
 1 kg-mole of fuel contains 0.166 kg-mole CO and 0.016 kg-mole O₂

The heat of combustion for 0.166 kg-mole CO = 0.166*(-67900) = -11271 Kcal

Heat Input

Heat Output

Decomposition heat of limestone (10*ΔH_{CaO}+1.13ΔH_{MgO})

Sensible heat in the fuel (X*ΔH₂₉₈⁴⁷³)

Calorific value of the fuel (-11271 X)

Sensible heat in CaO (10*ΔH₂₉₈¹¹⁷³)

Sensible heat in MgO (1.133*ΔH₂₉₈¹¹⁷³)

Sensible heat in off-gas ((10 + 0.238 X)* ΔH₂₉₈⁴⁷³ CO +

(0.74 X + 0.302 X)* ΔH₂₉₈⁴⁷³ N₂ +

(0.0134 X)* ΔH₂₉₈⁴⁷³ O₂ +

5.29* ΔH₂₉₈⁴⁷³ H₂O)

Material balance gives

$$\text{CO} = 10 + 0.238 X \quad \text{CaO} = 10$$

$$\text{N}_2 = 0.74 X + 0.302 X \quad \text{MgO} = 1.133$$

$$\text{O}_2 = 0.0134 X \quad \text{H}_2\text{O} = 5.29$$

Heat Input

Decomposition heat of limestone ($10 \cdot \Delta H_{CaO} + 1.13 \Delta H_{MgO}$)

Sensible heat in the fuel ($X \cdot \Delta H_{298}^{473}$)

Calorific value of the fuel ($-11271 X$)

Heat Output

Sensible heat in CaO ($10 \cdot \Delta H_{298}^{1173} CaO$)

Sensible heat in MgO ($1.133 \cdot \Delta H_{298}^{1173} MgO$)

Sensible heat in off-gas ($(10 + 0.238 X) \cdot \Delta H_{298}^{473} CO_2 +$

$(0.74 X + 0.302 X) \cdot \Delta H_{298}^{473} N_2 +$

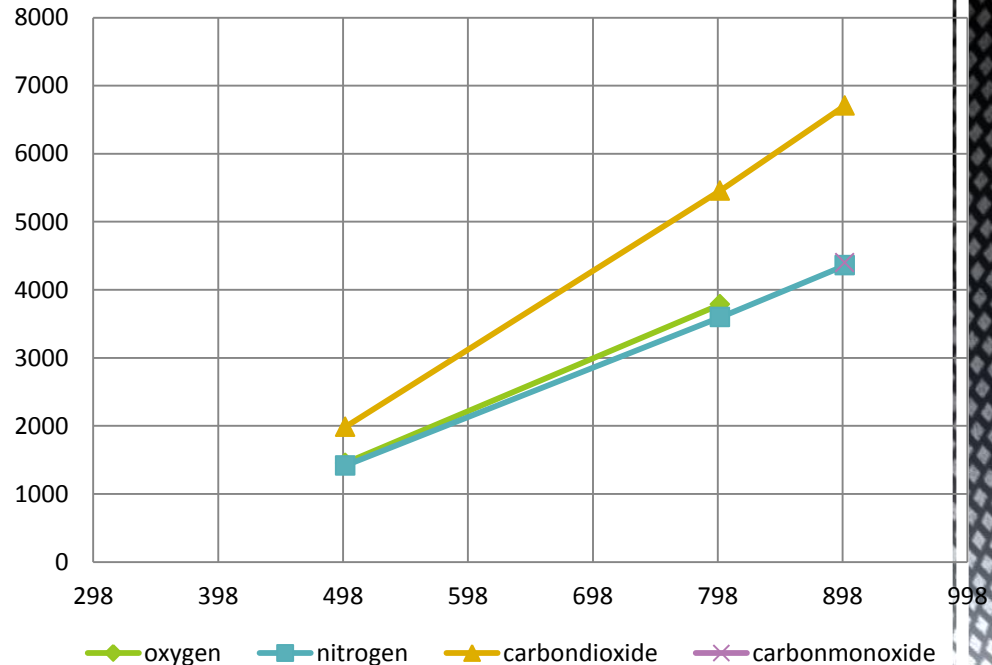
$(0.0134 X) \cdot \Delta H_{298}^{473} O_2 +$

$5.29 \cdot \Delta H_{298}^{473} H_2O$)



$C_p CaO = 49.622 + 4.519 \times 10^{-3} T - 6.945 \times 10^{-5} / T^2$

$C_p MgO = 48.995 + 3.138 \times 10^{-3} T - 11.715 \times 10^{-5} / T^2$



Cooling of flue gas

Flue gas is passed through a water heat boiler which cools it from 1121 C to 293 C

Calculate the heat given up by the flue gas

425 m³/min flue gas

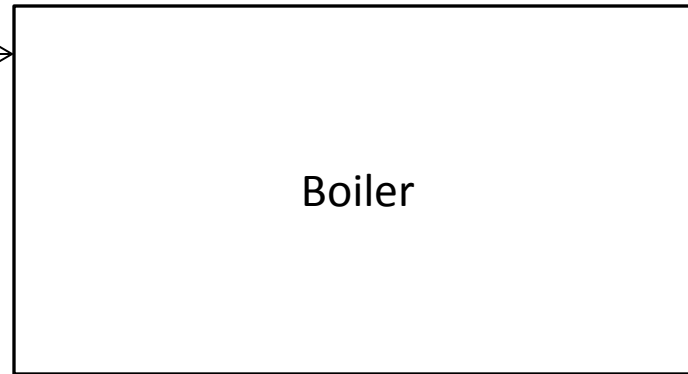
@ 1121 C, 1394 K

74% N₂

14% CO₂

10% H₂O

2% O₂



Flue gas

@ 293 C, 566 K

Basis: 425 m³

Reference temperature = 25 C

Pressure kg/cm ² (g)	Pressure Kg/cm ² (abs)	Pressure Bar (abs)	Temp °K	Temp °C	Sp. Vol (Steam) m ³ / kg	Density (Steam) kg / m ³	Enthalpy of Steam ' h _g ' kcal/kg	Enthalpy of Evap ' h _{fg} ' kcal/kg	Enthalpy of Water ' h _f ' Kcal/kg	Vapour Pressure Bar (a)	Dynamic Viscosity (10) ⁻⁶ Pa s
0	1.03	1.02	373.33	100.18	1.66	0.60	639.8	539.44	100.36	1.02	12.28
0.1	1.13	1.12	375.94	102.79	1.53	0.66	640.77	537.77	103.00	1.12	12.37
0.2	1.23	1.22	378.37	105.22	1.41	0.71	641.66	536.21	105.45	1.22	12.46
0.3	1.33	1.32	380.64	107.49	1.31	0.76	642.49	534.74	107.74	1.32	12.53
0.4	1.43	1.41	382.77	109.62	1.22	0.82	643.26	533.36	109.90	1.41	12.61
0.5	1.53	1.51	384.79	111.64	1.15	0.87	643.98	532.04	111.94	1.51	12.68
0.6	1.63	1.61	386.70	113.55	1.08	0.92	644.65	530.78	113.87	1.61	12.74
0.7	1.73	1.71	388.51	115.36	1.02	0.98	645.29	529.58	115.71	1.71	12.81
0.8	1.83	1.81	390.24	117.09	0.97	1.03	645.89	528.42	117.47	1.81	12.87
0.9	1.93	1.91	391.90	118.75	0.93	1.08	646.47	527.32	119.15	1.91	12.92
1.0	2.03	2.01	393.49	120.34	0.88	1.13	647.01	526.25	120.76	2.01	12.98

$$425 * 0.74 / 22.4 = 14.04 \text{ kg-mole/min N}_2$$

Heat Input for N₂

Sensible heat for 1121 to 25 C

$$14.04 * (H_{1394} - H_{298}) = 14.04 * 8305.5 = 116609 \text{ kcal}$$

Heat Output for N₂

Sensible heat for 25 to 293 C

$$14.04 * (H_{566} - H_{298}) = 14.04 * 1884 = 26451 \text{ kcal}$$

$$425 * 0.14 / 22.4 = 2.66 \text{ kg-mole/min CO}_2$$

Heat Input for CO₂

Sensible heat for 1121 to 25 C

$$2.66 * (H_{1394} - H_{298}) = 2.66 * 13277 = 35317 \text{ kcal}$$

Heat Output for CO₂

Sensible heat for 25 to 293 C

$$2.66 * (H_{566} - H_{298}) = 2.66 * 2711 = 7211 \text{ kcal}$$

$$425 * 0.1 / 22.4 = 1.90 \text{ kg-mole/min H}_2\text{O}$$

Heat Input for H₂O

Sensible heat for 1121 to 25 C

$$1.90 * (H_{1394} - H_{298}) = 1.90 * 10320 = 19608 \text{ kcal}$$

Heat Output for H₂O

Sensible heat for 25 to 293 C

$$1.90 * (H_{566} - H_{298}) = 1.90 * 2219 = 4216 \text{ kcal}$$

$$425 * 0.021 / 22.4 = 0.38 \text{ kg-mole/min O}_2$$

Heat Input for O₂

Sensible heat for 1121 to 25 C

$$0.38 * (H_{1394} - H_{298}) = 0.38 * 8783 = 3337 \text{ kcal}$$

Heat Output for O₂

Sensible heat for 25 to 293 C

$$0.38 * (H_{566} - H_{298}) = 0.38 * 1953 = 742 \text{ kcal}$$

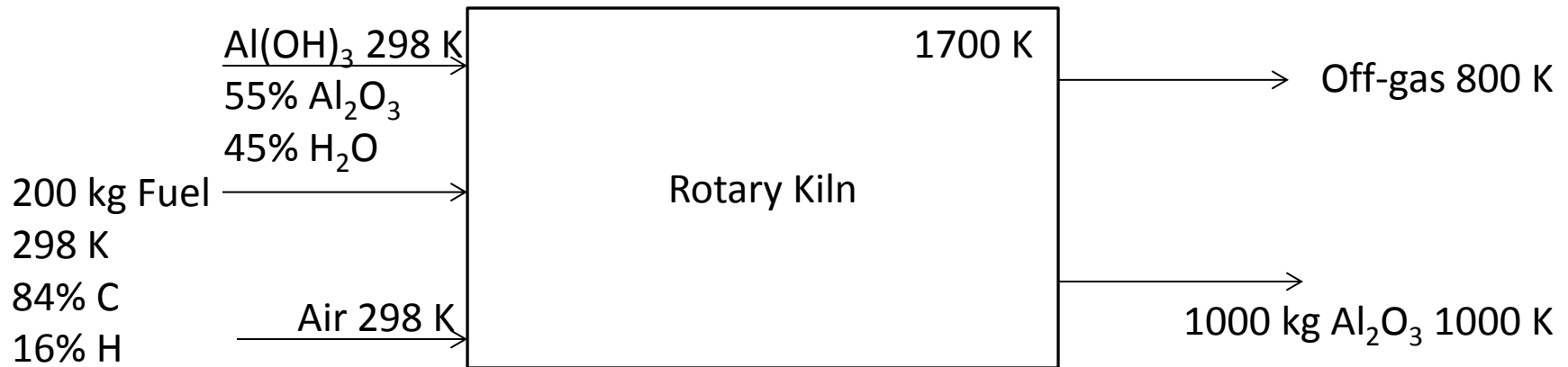
$$\text{Total Input} = 174871 \text{ kcal}$$

$$\text{Total Output} = 38620 \text{ kcal}$$

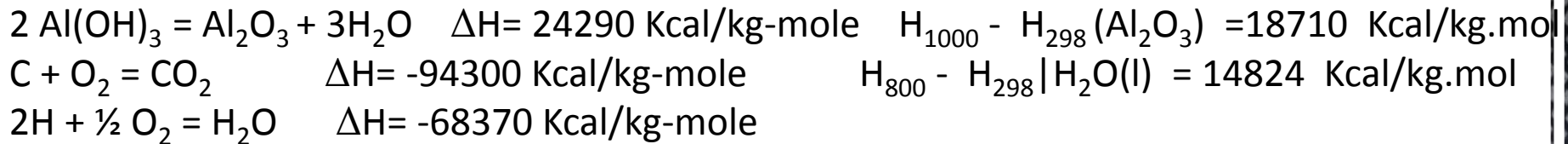
$$\text{Heat given up by the flue gas} = 174871 - 38620 = 136251 \text{ kcal}$$

Alumina calcination

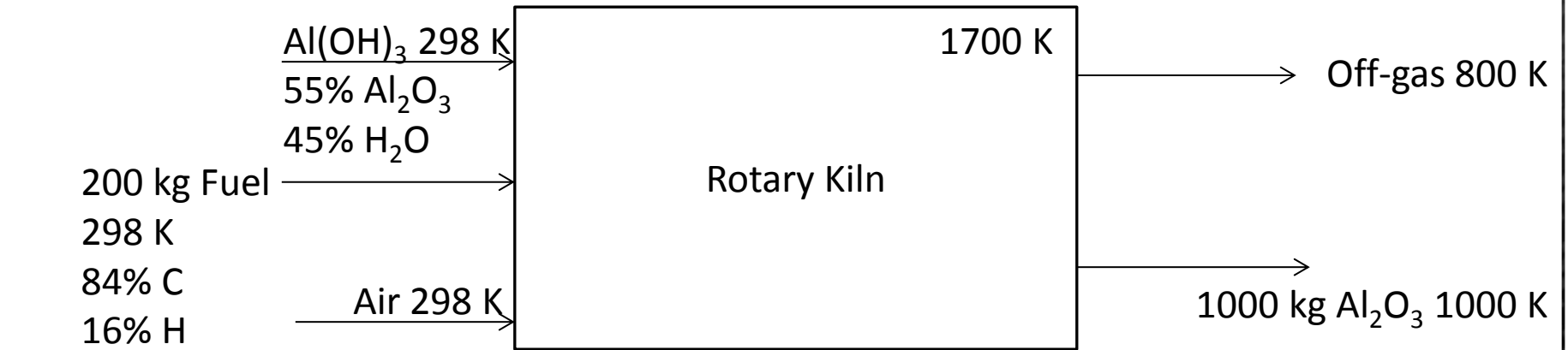
In the electrolysis, anhydrous alumina is required. For this purpose $\text{Al}(\text{OH})_3$ is calcined at 1700 K in rotary kiln. A kiln receives a damp filter cake of $\text{Al}(\text{OH})_3$ analyzing 55% Al_2O_3 and 45% total H_2O (free and combined) and produce, pure Al_2O_3 as solid product. The fuel consumption is estimated to be 0.2Kg of fuel oil of composition 84% C and 16% H per Kg of alumina. Air for combustion is 20% excess than theoretical required. Assume complete combustion and heat losses 10% of heat input.



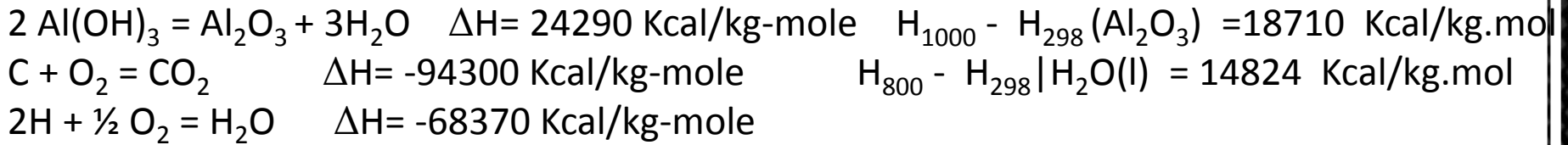
Reactions:



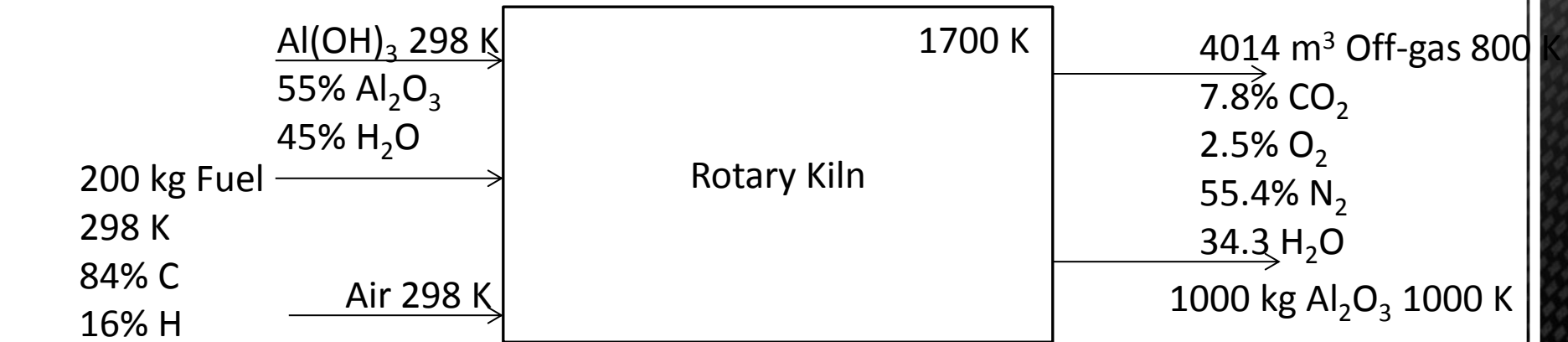
Calculate the volume of gases leaving the kiln per 1000 kg alumina



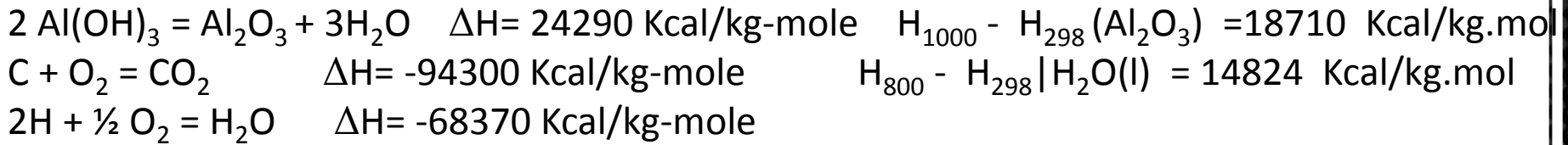
Reaction:



Calculate the volume of gases leaving the kiln per 1000 kg alumina



Reaction:



Perform the heat balance

Heat Input

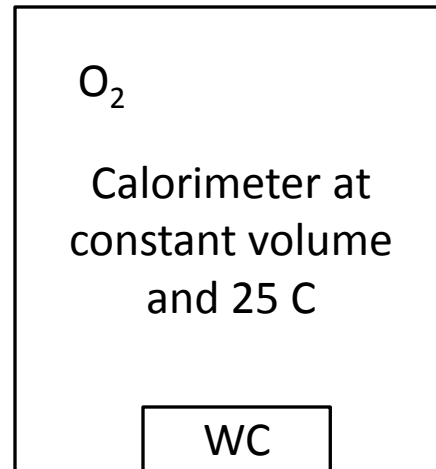
- Heat of alumina calcination
- Heat of combustion

Heat Output

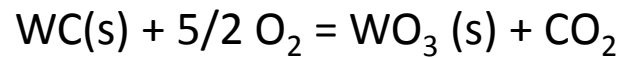
- Sensible heat in alumina
- Sensible heat in off-gas

Combustion

A sample of tungsten carbide, WC is burned to WO_3 and CO_2 using O_2 in a closed bomb calorimeter so that the combustion occurs at a constant volume. The calorimeter and its contents are at 25 C before combustion and are cooled back to the same temperature afterwards. The total heat evolved from the calorimeter during the combustion and subsequent cooling is 1454 calories/gram WC. Calculate the ΔH for the combustion reaction at 25 C and 1 atm per mole of WC and the heat of formation of WC from tungsten and graphite at 25 C. Consider the gases behaving as ideal gases and H and U are independent of pressure



Reaction:



Basis 1 g-mole WC

$$\Delta H_{298} = \Delta U + \Delta(PV)$$

$$\Delta H_{298} = \Delta U + \Delta(PV)$$

ΔU :

Total heat evolved in the calorimeter = 1454 cal/g WC

1 mole WC = 196 grams

Total heat evolved = 1454 * 196 = 285000 cal/mole WC

$\Delta U = Q - W$, at constant volume $\Delta U = Q = -285000$ cal/mole WC

$\Delta(PV)$:

$PV = nRT$, $\Delta PV = \Delta nRT$

$\Delta n = (\text{number of moles of } CO_2 - \text{number of moles of } O_2)$

$\Delta n = (1 - 5/2) = -3/2$ moles of gas

$\Delta(PV) = \Delta nRT = -3/2 * 1.987 * 298 = -888$ calories

$$\Delta H_{298} = \Delta U + \Delta(PV)$$

$$= -285000 - 888 = -285888 \text{ calories/g-mole WC}$$

$$\Delta H_{298} = \Sigma(\Delta H_f \text{ products}) - \Sigma(\Delta H_f \text{ reactants}) = \Delta H_f(WO_3) - \Delta H_f(CO_2) - \Delta H_f(WC)$$

$$\Delta H_f(WO_3) = -200840 \text{ cal/g-mole}, \Delta H_f(CO_2) = -94050 \text{ cal/g-mole}$$

$\Delta H_f(WC)$ is obtained from the calorimeter experiment as -9002 cal/g-mole