Jet and Rocket Propulsion

AE4451

LECTURE 10 class example

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Example problem

The following reaction describes the decomposition of the liquid monopropellant nitromethane into 5 different gaseous products :

$$CH_3NO_2 \rightarrow n_{CO}CO + n_{CO_2}CO_2 + n_{H_2}H_2 + n_{H_20}H_2O + n_{N_2}N_2$$

Using the water-gas reaction known to be written:

$$H_2 + CO_2 \rightarrow H_2O + CO$$

Determine the following:

(i) the number of moles of each product from the decomposition of nitromethane

(ii) the combustion temperature

species	$\Delta_f H^0$ (heat of formation)	Δh_j^{2500} (enthalpy change from reference to imposed T of 2500)
N_2	0	74.296
H_20	-241.826	99.108
H_2	0	70.498
CO	-110.53	74.985
CO_2	-393.522	121.917
CH_3NO_2	-113.1	

Example problem

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(1) let's start with the atom balance for this reaction:

$$CH_3NO_2 \rightarrow n_{CO}CO + n_{CO_2}CO_2 + n_{H_2}H_2 + n_{H_20}H_2O + n_{N_2}N_2$$

where n_x = number of moles of the subscripted compound *x*

- for each element, we check the numbers of atoms present on the left hand side (in the reactants), and compare this to the numbers of atoms found on the right hand side (in the products). This gives:

(i) C: $1 = n_{CO} + n_{CO_2}$

(ii) H: $3 = 2n_{H_2} + 2n_{H_2O}$

(iii) O: $2 = n_{CO} + 2n_{CO_2} + n_{H_2O}$

(iv) N: $1 = 2n_{N_2}$

- since *N* appears in only one product on the right hand side, we can see immediately from (iv) that

$$n_{N_2} = 0.5$$

Example problem

$$CH_3NO_2 \rightarrow n_{CO}CO + n_{CO_2}CO_2 + n_{H_2}H_2 + n_{H_20}H_2O + n_{N_2}N_2$$

(2) we now have 4 unknown mole ratios, an unknown combustion temperature, and 3 equations. We can use the water-gas reaction given in our problem statement to help.

- recall (Lecture 8) that we could write the equilibrium constant *Kp* in terms of partial pressures (or simply mole ratios).

  e.g. mole ratio of CO_2 in the products is given by $$\frac{n_{CO_2}}{n_{CO}CO + n_{CO_2}CO_2 + n_{H_2}H_2 + n_{H_20}H_2O + n_{N_2}N_2}$$

- for the given water-gas reaction, we can write: $$K_p(T) = \frac{n_{H_2O}n_{CO}}{n_{CO_2}n_{H_2}}$$

This gives us a 4th equation. We can in theory solve for the mole ratios, provided we specify a combustion temperature to use, which sets our K_p

Example problem

summary of our equations so far:

(i) $$1 = n_{CO} + n_{CO_2}$$

(ii) $$3 = 2n_{H_2} + 2n_{H_2O}$$

(iii) $$2 = n_{CO} + 2n_{CO_2} + n_{H_2O}$$

(iv) $$1 = 2n_{N_2}$$

(v) $$K_p n_{CO_2} n_{H_2} = n_{H_2O} n_{CO}$$

we can choose to solve for any of the unknowns, e.g. n_{H_2O}

(iii) – (i) gives $1 = n_{CO_2} + n_{H_2O}; \quad n_{CO_2} = 1 - n_{H_2O}$

from (i): $n_{CO} = 1 - n_{CO_2} = n_{H_2O}$ i.e. same number of moles of CO and H_2O

and from (ii): $n_{H_2} = \frac{3}{2} - n_{H_2O}$

(v) can be written $K_p n_{CO_2} n_{H_2} = n_{H_2O}{}^2$

Example problem

substituting to leave (v) only in terms of moles of H_2O:

$$K_p n_{CO_2} n_{H_2} = n_{H_2O}{}^2$$

$$K_p(1-n_{H_2O})\left(\frac{3}{2}-n_{H_2O}\right) = n_{H_2O}{}^2$$

$$n_{H_2O}{}^2\left(\frac{1}{K_p}-1\right)+2.5n_{H_2O}-1.5=0$$

The temperature 2500 K corresponds to a K_p value of 6.440 for the water-gas reaction (this will be given to you)

substituting our K_p value and solving the above quadratic equation gives us

$$n_{H_2O} = \cancel{2.123}, 0.836$$

(obviously, we can only use the root which is < 1)

$$\Rightarrow n_{CO} = 0.836$$

$$\Rightarrow n_{CO_2} = 0.164 \Rightarrow n_{H_2} = 0.664$$

and from our atom balance equations, we had already found that $n_{N_2} = 0.5$

Example problem

(3) Now that we have these values, we can verify the validity of the temperature we imposed, by checking that the heat of our reaction (calculated with the moles we determined) matches the enthalpy rise

$$\Delta_r H^0 = \Sigma(n\Delta_f H^0)_{\text{products}} - \Sigma(n\Delta_f H^0)_{\text{reactants}}$$

overall heat of reaction — i.e. formation enthalpies x number of moles *n*

species	$\Delta_f H^0$	n
N_2	0	0.500
H_20	-241.826	0.836
H_2	0	0.664
CO	-110.53	0.836
CO_2	-393.522	0.164
CH_3NO_2	-113.1	1

$$\Delta_r H^0 = \left[\underbrace{(0.5 \text{ x } 0)}_{N_2} + \underbrace{(0.836 \text{ x } -241.826)}_{H_20} + \underbrace{(0.664 \text{ x } 0)}_{H_2} + \underbrace{(0.836 \text{ x } -110.53)}_{CO} + \underbrace{(0.164 \text{ x } -393.522)}_{CO_2} \right] - \underbrace{(1\text{x } -113.1)}_{CH_3NO_2}$$

$\Delta_r H^0$ = 246 KJ/mol

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(4) We can calculate the enthalpy rise using the JANAF tables as well, at the temperature 2500 K

overall enthalpy rise $\Delta H_{298}^{2500} = \Sigma n_j \Delta h_j$

i.e. enthalpy change for our product species going from reference temp 298 K to 2500 K, x number of moles *n*

species	Δh_j^{2500}	n_f
N_2	74.296	0.500
H_20	99.108	0.836
H_2	70.498	0.664
CO	74.985	0.836
CO_2	121.917	0.164
CH_3NO_2		1

$$\Delta H_{298}^{2500} = (0.5 \text{ x } 74.296) + (0.836 \text{ x } 99.108) + (0.664 \text{ x } 70.498) + (0.836 \text{ x } 74.985) + (0.164 \text{ x } 121.917)$$

(N_2, H_20, H_2, CO, CO_2)

ΔH_{298}^{2500} = 249.49 KJ/mol

Example problem

Notice how

$$\Delta_r H^0 \neq \Delta H_{298}^{2500}$$

246 KJ/mol 249.49 KJ/mol

- in other words, our guess of 2500 K was too high
- we need choose a lower temperature and re-do the process until $\Delta_r H^0 = \Delta H_{298}^{2500}$

This will ultimately give us the desired combustion temperature.

In your exam problems, you'll not be expected to perform the next iteration steps by hand, but I do want you to understand the significance of such calculations. We will need them in determining the performance of propulsion systems where such reactions are expected.