

Question 1:

Use stoichiometry to create balanced chemical reactions for the following fuels + air:
methane, ethane, propane, butane, pentane, hexane, methyl decanoate ($C_{11}H_{22}O_2$),
unknown carbohydrate ($C_xH_yO_z$)

Answer 1:

Methane is CH_4

Starting Equation: $CH_4 + a*O_2 = b*CO_2 + c*H_2O$

Balance C: $1 = b$

Balance H: $4 = 2*c$

Balance O: $2*a = 2*b + c$

Final Equation: $CH_4 + 2*O_2 = 1*CO_2 + 2*H_2O$

Ethane is C_2H_6

Starting Equation: $C_2H_6 + a*O_2 = b*CO_2 + c*H_2O$

Balance C: $2 = b$

Balance H: $6 = 2*c$

Balance O: $2*a = 2*b + c$

Final Equation: $CH_4 + (7/2)*O_2 = 2*CO_2 + 3*H_2O$

Propane is C_3H_8

Starting Equation: $C_3H_8 + a*O_2 = b*CO_2 + c*H_2O$

Balance C: $3 = b$

Balance H: $8 = 2*c$

Balance O: $2*a = 2*b + c$

Final Equation: $CH_4 + 5*O_2 = 3*CO_2 + 4*H_2O$

Butane is C_4H_{10}

Starting Equation: $C_4H_{10} + a*O_2 = b*CO_2 + c*H_2O$

Balance C: $4 = b$

Balance H: $10 = 2*c$

Balance O: $2*a = 2*b + c$

Final Equation: $CH_4 + (13/2)*O_2 = 4*CO_2 + 5*H_2O$

Pentane is C_5H_{12}

Starting Equation: $C_5H_{12} + a*O_2 = b*CO_2 + c*H_2O$

Balance C: $5 = b$

Balance H: $12 = 2*c$

Balance O: $2*a = 2*b + c$

Final Equation: $CH_4 + 8*O_2 = 5*CO_2 + 6*H_2O$

Hexane is C_6H_{14}

Starting Equation: $C_6H_{14} + a*O_2 = b*CO_2 + c*H_2O$

Balance C: $6 = b$

Balance H: $14 = 2*c$

Balance O: $2*a = 2*b + c$

Final Equation: $CH_4 + (19/2)*O_2 = 6*CO_2 + 7*H_2O$

Methyl Decanoate is $C_{11}H_{22}O_2$

Starting Equation: $C_{11}H_{22}O_2 + a*O_2 = b*CO_2 + c*H_2O$

Balance C: $11 = b$

Balance H: $22 = 2*c$

Balance O: $2+2*a = 2*b + c$

Final Equation: $CH_4 + (31/2)*O_2 = 11*CO_2 + 11*H_2O$

Unknown Carbohydrate is $C_xH_yO_z$

Starting Equation: $C_xH_yO_z + a*O_2 = b*CO_2 + c*H_2O$

Balance C: $x = b$

Balance H: $y = 2*c$

Balance O: $z+2*a = 2*b + c$

Final Equation: $CH_4 + (x + \frac{y}{4} - \frac{z}{2})*O_2 = x*CO_2 + (y/2)*H_2O$

Question 2:

Given hydrogen gas (H_2) and air with “fuel-air equivalence ratio” $\phi = (1/2)$, calculate mole (X) and mass fractions (Y) of all product species, average molecular weight, and average specific heat ($\bar{c}_{p,ave}$) at $P=1\text{atm}$ $T=298.15\text{K}$ (standard state).

Answer 2:

Definition of “fuel-air equivalence ratio”

$$\phi = \frac{\text{fuel-to-oxidizer ratio}}{(\text{fuel-to-oxidizer ratio})_{st}} = \frac{m_{fuel}/m_{ox}}{(m_{fuel}/m_{ox})_{st}} = \frac{n_{fuel}/n_{ox}}{(n_{fuel}/n_{ox})_{st}}$$

Where: m represents the mass, n represents number of moles, and suffix “st” stands for stoichiometric conditions.

Definition of mass fraction is:

$$Y_i = \frac{m_i}{m_{tot}} \quad m_{tot} = \sum_{i=1}^N m_i \quad \sum_{i=1}^N Y_i = 1$$

Where N is the number of species and $m_i = W_i * n_i$.

Definition of mole fraction is:

$$X_i = \frac{n_i}{n_{tot}} \quad n_{tot} = \sum_{i=1}^N n_i \quad \sum_{i=1}^N X_i = 1$$

Air consists of 1 mole O_2 for every 3.76 mole of N_2 .

Molecular weight (W) of O₂ is 32 kg/kmol, H₂ is 2 kg/kmol, and N₂ is 28 kg/kmol.

Note: specific heat, \bar{c}_p , is a function of both pressure and temperature.
(Also: \bar{c}_v , is a function of both specific volume and temperature.)

At T=298 K and P=1atm: \bar{c}_p of O₂ = 29.315 $\frac{kJ}{kmol*K}$, \bar{c}_p of H₂ = 28.871 $\frac{kJ}{kmol*K}$,
and \bar{c}_p of N₂ = 29.071 $\frac{kJ}{kmol*K}$

Where the line over \bar{c}_p indicates mole-based values.

The stoichiometric reaction for H₂ and air is: 2*H₂ + O₂ = 2*H₂O

$$\left(\frac{n_{fuel}}{n_{ox}}\right)_{st} = \left(\frac{n_{H_2}}{n_{O_2}}\right)_{st} = 2$$

Therefore

$$\left(\frac{n_{H_2}}{n_{O_2}}\right) = phi * \left(\frac{n_{H_2}}{n_{O_2}}\right)_{st} = 0.5 * 2 = 1$$

The mixture is 1 mole of H₂, 1 mole of O₂, 3.76 moles of N₂.

$$m_{tot} = \sum_{i=1}^N W_i * n_i = 2 * 1 + 32 * 1 + 28 * 3.76 = 139.28 \text{ kg}$$

$$Y_{H_2} = \frac{m_{H_2}}{m_{tot}} = \frac{2 * 1}{139.28} = 0.0144$$

$$Y_{O_2} = \frac{m_{O_2}}{m_{tot}} = \frac{32 * 1}{139.28} = 0.2298$$

$$Y_{N_2} = \frac{m_{N_2}}{m_{tot}} = \frac{28 * 3.76}{139.28} = 0.7559$$

$$\sum_{i=1}^N Y_i = 1.0001 \quad (slight \ error \ from \ rounding)$$

$$n_{tot} = \sum_{i=1}^N n_i = 1 + 1 + 3.76 = 5.76$$

$$X_{H_2} = \frac{n_{H_2}}{n_{tot}} = \frac{1}{5.76} = 0.1736$$

$$X_{O_2} = \frac{n_{O_2}}{n_{tot}} = \frac{1}{5.76} = 0.1736$$

$$X_{N_2} = \frac{n_{N_2}}{n_{tot}} = \frac{3.76}{5.76} = 0.6528$$

$$\sum_{i=1}^N X_i = 1.0 \quad (no \ error \ from \ rounding)$$

$$W_{ave} = \frac{m_{tot}}{n_{tot}} = \sum_{i=1}^N W_i * X_i = 24.18 \frac{kg}{kmol}$$

$$\bar{c}_{p_{ave}} = \sum_{i=1}^N \bar{c}_{p_i} * X_i = 29.0786 \frac{kJ}{kmol * K}$$

Question 3:

From the ideal gas law and first law of thermodynamics derive the isentropic relations for pressure and temperature.

Answer 3:

$$\text{Ideal gas law: } PV = nR_u T \quad V/m = v \quad n = m/M \quad Pv = \frac{R_u}{M} T \quad R = R_{\text{specific}} = \frac{R_u}{M}$$

Where M is molecular weight of mixture in units kg/kmol .

R_u is universal gas constant with cgs units $\frac{\text{erg}}{\text{K*mol}}$

Ideal gas law becomes: $Pv=RT$

Taking natural log of both sides: $\ln(P) + \ln(v) = \ln(R) + \ln(T)$

Taking derivative, that is multiplying equation by "d" (Note: $d(\ln R)=0$):

$$d(\ln P) + d(\ln v) = d(\ln T) \quad [\text{eq A}]$$

First law of thermodynamics is conservation of energy

$$dU = dQ + dW \quad dW = -PdV \quad dU = c_v dT \quad dQ = TdS$$

Definition of isentropic: adiabatic (no heat transfer) and reversible process

Definition of reversible: process can be reversed with out dissipation of energy (entropy production), therefore there is no change in entropy of system.

Note relationship between specific heats and universal gas constant:

$$(\text{mole based}) \quad \bar{c}_p - \bar{c}_v = R_u$$

$$(\text{mass based}) \quad c_p - c_v = R_u/M = R_{\text{specific}} = R$$

First law becomes (Note: $TdS = 0$ because reversible system):

$$c_v dT = -Pdv = -Pv \frac{dv}{v} = -RTd(\ln v)$$

Where we used the definition of natural log: $\int \frac{dv}{v} = \ln v \Rightarrow \frac{dv}{v} = d(\ln v)$

From this equation we solve for $d(\ln v)$:

$$d(\ln v) = -\frac{c_v}{R} \frac{dT}{T} = -\frac{c_v}{R} d(\ln T) \quad [\text{eq B}]$$

Substituting eq B into eq A, and manipulate, (note: heat capacity ratio, $k=c_p/c_v$) :

$$d(\ln P) = \frac{c_v}{R} d(\ln T) + d(\ln T)$$

$$d(\ln P) = \left(\frac{c_v}{R} + 1 \right) d(\ln T)$$

$$d(\ln P) = \frac{c_p}{R} d(\ln T)$$

$$d(\ln P) = \frac{c_p}{c_p - c_v} d(\ln T)$$

$$d(\ln P) = \frac{k c_v}{k c_v - c_v} d(\ln T) = \frac{k}{k-1} d(\ln T) \quad [eq\ C]$$

Using property of natural logs, we can move $\frac{k}{k-1}$ term:

$$d(\ln P) = d \left[\ln \left(T^{\frac{k}{k-1}} \right) \right]$$

Now integrate from state 1 to state 2:

$$\int_1^2 d(\ln P) = \int_1^2 d \left[\ln \left(T^{\frac{k}{k-1}} \right) \right]$$

$$\ln P_2 - \ln P_1 = \ln \left(T_2^{\frac{k}{k-1}} \right) - \ln \left(T_1^{\frac{k}{k-1}} \right)$$

$$\ln \left(\frac{P_2}{P_1} \right) = \ln \left[\left(\frac{T_2}{T_1} \right)^{\frac{k}{k-1}} \right]$$

Finally resulting in

$$\frac{P_2}{P_1} = \left(\frac{T_2}{T_1} \right)^{\frac{k}{k-1}}$$

Question 4:

From the ideal gas law and first law of thermodynamics derive the isentropic relations for pressure and specific volume.

Answer 4:

Substituting eq C into eq A of question 3, and manipulate:

$$d(\ln P) + d(\ln v) = \frac{k-1}{k} d(\ln P)$$

$$\left(\frac{k-1}{k} - 1 \right) d(\ln P) = d(\ln v)$$

$$\frac{-1}{k} d(\ln P) = d(\ln v)$$

$$d(\ln P) = -k d(\ln v)$$

Using property of natural logs, we can move $-k$ term:

$$d(\ln P) = d[\ln(v^{-k})]$$

Now integrate from state 1 to state 2:

$$\int_1^2 d(\ln P) = \int_1^2 d[\ln(v^{-k})]$$

$$\ln P_2 - \ln P_1 = \ln(v_2^{-k}) - \ln(v_1^{-k})$$

$$\ln \frac{P_2}{P_1} = \ln \left[\left(\frac{v_2}{v_1} \right)^{-k} \right]$$

$$\frac{P_2}{P_1} = \left(\frac{v_2}{v_1}\right)^{-k}$$

Finally resulting in

$$\frac{P_2}{P_1} = \left(\frac{v_1}{v_2}\right)^k$$

Question 5:

From definition of entropy, $dS=dQ/T$, isentropic relations, ideal gas law and first law of thermodynamics derive the equation that calculates entropy given a change in pressure, and given the value of entropy at standard state pressure P^0 , that is:

$$S(T, P) = S(T, P^0) - R_u \ln\left(\frac{P}{P^0}\right)$$

Answer 5:

(Note: for R_u to be used S must be molar entropy. If R is used then S is mass entropy)

Question 5:

Derive the entropy change of ideal gases, using definitions of enthalpy ($h=u+Pv$) and entropy ($ds=dq/T$), first law of thermodynamics, and property relations for an ideal gas (ideal gas law, definitions of specific heats c_p and c_v)

$$s_2 - s_1 = \int_1^2 c_v \frac{dT}{T} + R \ln \frac{v_2}{v_1} \quad \text{units: } \frac{kJ}{kg * K}$$

$$s_2 - s_1 = \int_1^2 c_p \frac{dT}{T} - R \ln \frac{P_2}{P_1} \quad \text{units: } \frac{kJ}{kg * K}$$

If there is no temperature change this results in the following equations, where $s(T, P^0)$ is the value of entropy at temperature T and standard state pressure P^0 :

$$s(T, P) = s(T, P^0) + R \ln\left(\frac{v}{v^0}\right)$$

$$s(T, P) = s(T, P^0) - R \ln\left(\frac{P}{P^0}\right)$$

Note: entropy changes can be expressed on a unit-mole basis by multiplying by molecular weight of mixture (M_{mix} has units of kg/kmol):

$$\bar{s}_2 - \bar{s}_1 = \int_1^2 \bar{c}_v \frac{dT}{T} + R_u \ln \frac{v_2}{v_1} \quad \text{units: } \frac{kJ}{kmol * K}$$

$$\bar{s}_2 - \bar{s}_1 = \int_1^2 \bar{c}_p \frac{dT}{T} - R_u \ln \frac{P_2}{P_1} \quad \text{units: } \frac{kJ}{kmol * K}$$

If there is no temperature change this results in the following equations, where $\bar{s}(T, P^0)$ is the value of entropy at temperature T and standard state pressure P^0 :

$$\bar{s}(T, P) = \bar{s}(T, P^0) + R_u \ln\left(\frac{v}{v^0}\right)$$

$$\bar{s}(T, P) = \bar{s}(T, P^0) - R_u \ln\left(\frac{P}{P^0}\right)$$

Answer 5:

Definition of first law of thermodynamics

$$du = dq + dw \quad \text{where: } dw = -Pdv \quad \text{and} \quad dq = Tds$$

Solving for ds:

$$ds = \frac{du}{T} + \frac{Pdv}{T}$$

Substitute $du=c_vdT$ and $P=RT/v$:

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}$$

Integrate between state 1 and state 2, to obtain

$$s_2 - s_1 = \int_1^2 c_v \frac{dT}{T} + R \ln \frac{v_2}{v_1}$$

Now to find equation with pressure instead of specific volume, start with definition of enthalpy:

$$h = u + Pv$$

And differentiate:

$$dh = du + Pdv + vdp$$

Substitute first law of thermodynamics and solve for ds:

$$ds = \frac{dh}{T} - \frac{vdp}{T}$$

Substitute $dh=c_pdT$ and $v=RT/P$:

$$ds = c_p \frac{dT}{T} - R \frac{dp}{P}$$

Integrate between state 1 and state 2, to obtain

$$s_2 - s_1 = \int_1^2 c_p \frac{dT}{T} - R \ln \frac{P_2}{P_1}$$

Additional note: the terms $\int_1^2 c_v \frac{dT}{T}$ or $\int_1^2 c_p \frac{dT}{T}$ can be simplified by assuming a constant average c_v or c_p value.

$$\begin{aligned} \int_1^2 c_v \frac{dT}{T} &\approx c_{v,ave} \ln \frac{T_2}{T_1} \\ \int_1^2 c_p \frac{dT}{T} &\approx c_{p,ave} \ln \frac{T_2}{T_1} \end{aligned}$$