
Example 1

Determine the entropy generated during the oxidation of glucose within the cells of the human body assuming that the reaction occurs at 310 K. Assume that steady state conditions apply, the entropy of glucose at 310 K is $288.96 \text{ kJ kmole}^{-1} \text{ K}^{-1}$, the inlet conditions are 300 K and 1bar, and 400% excess air is involved.

Solution

The overall reaction can be expressed as



where $\bar{q} = 2.5 \times 10^6 \text{ kJ kmole}^{-1}$ of glucose (from previous examples). At steady state

$$\bar{\sigma} = (\sum \bar{v}_k \hat{s}_k)_i + \sum (\bar{q}_j / T_{b,j}) + (\sum \bar{v}_k \hat{s}_k)_e \quad \text{(A)}$$

Recall that $\bar{s}_k^\circ(T) = \hat{s}_k(T, p_k)$. Therefore, for the species on the LHS of Eq. (A)

$$(\sum \bar{v}_k \hat{s}_k)_i = 1 \times 288.96 + 30 \times 218.01 + 30 \times 3.76 \times 193.4662 = 28663.33 \text{ kJ K}^{-1} \text{ kmole}^{-1} \text{ glucose.} \quad \text{(B)}$$

At the exit (species on the RHS of Eq. (A'))

$$X_{\text{O}_2} = 24 / 148.8 = 0.161, X_{\text{N}_2} = 0.758, X_{\text{CO}_2} = 0.0403, \text{ and } X_{\text{H}_2\text{O}} = 0.0403.$$

Hence,

$$\begin{aligned} \bar{s}_{\text{O}_2}(310\text{K}, p_{\text{O}_2}) &= 205.066 - 8.314 \times \ln(1 \times 0.16) = 220.2 \text{ kJ kmole}^{-1} \text{ K}^{-1}, \\ \bar{s}_{\text{N}_2} &= 193.8 \text{ kJ kmole}^{-1} \text{ K}^{-1}, \bar{s}_{\text{CO}_2} = 240.4 \text{ kJ kmole}^{-1} \text{ K}^{-1}, \text{ and} \\ \bar{s}_{\text{H}_2\text{O}} &= 215.5 \text{ kJ kmole}^{-1} \text{ K}^{-1}, \text{ i.e.,} \end{aligned}$$

$$(\sum \bar{v}_k \hat{s}_k)_e = 6 \times 213.7 + 6 \times 238.6 + 24 \times 220 + 112.8 \times 193.9 = 28483.71 \text{ kJ kmole}^{-1} \text{ of glucose} \quad \text{(C)}$$

Using Eq. (A) and specifying the control volume boundary just inside the human skin,

$$\bar{\sigma} = 2.5 \times 10^6 / 310 - 28633 + 28483.7 = 7915 \text{ kJ K}^{-1} \text{ kmole}^{-1} \text{ of glucose.}$$

Remarks

Entropy is generated since the inhalation temperature is different from the exhalation temperature, and due to the irreversible chemical reaction.

If $T_b = T_e = T_I = 37 \text{ C}$, entropy generation will be due to chemical irreversibilities alone.

The typical consumption of glucose is 0.31 g min^{-1} for a 65 kg person. Therefore, the entropy generated per second due to that person's irreversible metabolic rate is $43.92 \times 0.31 / (1000 \times 60) = 2.27 \times 10^{-4} \text{ kW K}^{-1}$ or $3.5 \times 10^{-6} \text{ kW kg}^{-1} \text{ K}^{-1}$. This number is typically higher for smaller-sized animal species.

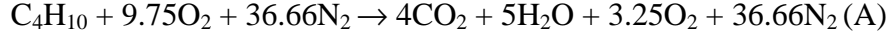
Example 2

1 kmole of butane enters a steady state steady flow reactor at 298 K and 250 kPa with 50% excess air. Combustion is assumed to be complete, and the products leave the reactor at 1000 K and 250 kPa. Determine the heat transfer, reactant and product entropies, the absolute availability of the reactants and products, the

entropy change between the exit and inlet, the entropy generation, the optimum work and the irreversibility.

Solution

The overall reaction can be expressed as



The reaction coefficients are

$$v_{\text{CO}_2} = (\text{N}_{\text{CO}_2}/\text{N}_{\text{F}})_e = 4, v_{\text{H}_2\text{O}} = 5, v_{\text{N}_2} = 36.66, \text{ and}$$

$$v_{\text{N}_2} = 36.66 \text{ and } v_{\text{O}_2} = 9.75.$$

The energy equation is

$$dE_{\text{cv}}/dt = \dot{Q}_{\text{cv}} - \dot{W}_{\text{cv}} + \sum_{k,i} \dot{N}_k \bar{e}_{T,k} - \sum_{k,e} \dot{N}_k \bar{e}_{T,k} \quad \text{(B)}$$

neglecting the kinetic and potential energies, we obtain the expression

$$(1/\dot{N}_{\text{F}}) dU_{\text{cv}}/dt = \bar{q} - \bar{w} + (\sum \bar{v}_k \hat{h}_k)_i - (\sum \bar{v}_k \hat{h}_k)_e.$$

At steady state and ideal gas conditions, $\hat{h}_k = \bar{h}_k$, and since $\bar{w} = 0$, we have the simplified relation

$$\bar{q} + (\sum \bar{v}_k \hat{h}_k)_i - (\sum \bar{v}_k \hat{h}_k)_e = 0, \text{ i.e.} \quad \text{(C)}$$

$$\bar{q} = H_{\text{P}} - H_{\text{R}}, \text{ where} \quad \text{(D)}$$

$$H_{\text{P}} = (\sum \bar{v}_k \hat{h}_k)_e \text{ and } H_{\text{R}} = (\sum \bar{v}_k \hat{h}_k)_i. \quad \text{(E)}$$

$H_{\text{R}} = -126148 \text{ kJ kmole}^{-1}$ of C_4H_{10} , and

$$H_{\text{P}} = 4 \times (-393,520 + 33,425) + 5 \times (-241,827 + 25,978) + 3.25 \times (22,707) + 36.66 \times (21,460) = -1,659,104 \text{ i.e.,}$$

$$\bar{q} = H_{\text{P}} - H_{\text{R}} = -1533044 \text{ kJ kmole}^{-1} \text{ of } \text{C}_4\text{H}_{10}.$$

Likewise, we may show that

$$S_{\text{R}} = (\sum \bar{v}_k \hat{s}_k)_i = 9212.3 \text{ kJ kmole}^{-1} \text{ of fuel } \text{K}^{-1},$$

$$\Psi_{\text{R}} = (\sum \bar{v}_k \bar{\psi}_k)_i = -2869892 \text{ kJ kmole}^{-1} \text{ of fuel,}$$

$$S_{\text{P}} = (\sum \bar{v}_k \hat{s}_k)_e = 11363.7 \text{ kJ kmole}^{-1} \text{ of fuel } \text{K}^{-1},$$

$$\Psi_{\text{P}} = (\sum \bar{v}_k \bar{\psi}_k)_e = -5045283 \text{ kJ kmole}^{-1} \text{ of fuel } \text{K}^{-1}, \text{ and}$$

$$S_{\text{P}} - S_{\text{R}} = 11363.7 - 9212.3 = 2154.5 \text{ kJ kmole}^{-1} \text{ of fuel } \text{K}^{-1}.$$

Note that $\hat{s}_k = \bar{s}_k^\circ - \bar{R} \ln(p_k/1)$, $p_k = X_k P$

Applying the entropy balance equation for a steady state steady flow process,

$$(1/\dot{N}_{\text{F}}) dS_{\text{cv}}/dt = (\sum \bar{v}_k \hat{s}_k)_i + \sum (\bar{q}_j/T_{b,j}) - (\sum \bar{v}_k \hat{s}_k)_e + \bar{\sigma},$$

$$\bar{\sigma} = S_{\text{P}} - S_{\text{R}} - \sum (\bar{q}_j/T_{b,j}). \quad \text{(F)}$$

Using the values $T_b = 298 \text{ K}$ and $\bar{q} = -1533044 \text{ kJ}$,

$$\bar{\sigma} = 11363.7 - 9212.3 - (-1533044)/298 = 7294 \text{ kJ kmole}^{-1} \text{ of fuel } \text{K}^{-1}.$$

The optimum work relation is

$$(1/\dot{N}_{\text{F}}) d(E_{\text{cv}} - T_o S_{\text{cv}})/dt = (\sum \bar{v}_k \bar{\psi}_k)_i + \sum \bar{q}_{\text{R},j} (1 - T_o/T_{\text{R},j}) - (\sum \bar{v}_k \bar{\psi}_k)_e - \bar{w} - \dot{i}.$$

Under steady state conditions if there is no thermal reservoir, then

$$\bar{w}_{\text{opt}} = \bar{\Psi}_R - \bar{\Psi}_P, \text{ where } \bar{\Psi}_R = (\sum \bar{v}_k \bar{\psi}_k)_R, \text{ and } \bar{\Psi}_P = (\sum \bar{v}_k \bar{\psi}_k)_E, \text{ i.e.,} \quad (\text{G})$$

$$\bar{w}_{\text{opt}} = 2175291 \text{ kJ kmole}^{-1} \text{ of } \text{C}_4\text{H}_{10}.$$

Therefore,

$$\dot{i} = \bar{w}_{\text{opt}} - \bar{w}_{\text{cv}} = 2175291 \text{ kJ kmole}^{-1} \text{ of } \text{C}_4\text{H}_{10}, \text{ since } \bar{w}_{\text{cv}} = 0.$$

The reactant properties at 2.5 bar and 298K are provided in the following table.

Units for p_k are in bar, \bar{h} in kJ kmole^{-1} , and the entropies in $\text{kJ kmole}^{-1} \text{K}^{-1}$.

Reactants	\bar{v}_k	\bar{h}	X_k	$p_k = X_k P$	\hat{s}	\bar{s}_k°	$(\bar{h} - T_o \hat{s})_k$
C_4H_{10}	1	-126148	0.021	0.0527	310.2	334.7	-225887
O_2	9.75	0	0.2057	0.5141	205.1	210.7	-62781
N_2	36.66	0	0.7733	1.933	191.6	186.1	-55428
Products							
CO_2	4	-360470	0.0818	0.205	269.3	282.5	-444302
$\text{H}_2\text{O}(\text{g})$	5	-215849	0.1022	0.256	232.7	244.0	-288561
O_2	3.25	22707	0.0665	0.166	243.6	258.5	-54326
N_2	36.66	21460	0.7495	1.874	228.2	222.9	-44973

Example 3

Consider that fuel and air enter an automobile engine at 298 K and 1 bar (state 1), and the car exhaust exits at the same pressure, but at 400 K (state 2). Assume complete combustion with 20% excess air. Show that

$$\bar{w} = \bar{\Psi}_R - \bar{\Psi}_P - \dot{i} - P \bar{v}_F, \text{ kJ kmole}^{-1} \text{ of burnt fuel} \quad (\text{A})$$

Determine the optimum work per kmole of burned liquid octane (C_8H_{18}).

Solution

The mass of the automobile is variable, since the liquid fuel weight in the fuel tank decreases over time due to fuel consumption. Hence, this is an unsteady problem. Assume that the species in the exhaust are CO_2 , H_2O , O_2 , and N_2 . From the availability balance relation

$$d\{E_{\text{cv}} - T_o S_{\text{cv}}\}/dt = \sum \dot{Q}_{R,j} (1 - \frac{T_o}{T_{R,j}}) + \{\sum \dot{N}_k \bar{\psi}_k\}_i - \{\sum \dot{N}_k \bar{\psi}_k\}_e - \dot{W}_{\text{cv}} - \dot{i} \quad (\text{B})$$

Consider the system control surface to exist around the automobile where $T_R = T_o$. Neglecting the kinetic and potential energies and considering an adiabatic car, Eq. (B) simplifies to the form

$$d(U_{\text{cv}} - T_o S_{\text{cv}})/dt = \{\sum \dot{N}_k \bar{\psi}_k\}_i - \{\sum \dot{N}_k \bar{\psi}_k\}_e - \dot{W}_{\text{cv}} - \dot{i} \quad (\text{C})$$

Since $U_{\text{cv}} = N_F \bar{u}_F$ and $S_{\text{cv}} = N_F \bar{s}_F$ and \bar{u}_F and \bar{s}_F are constants, then

$$d\{N_F(\bar{u}_F - T_o \bar{s}_F)\}/dt = +\{\sum \dot{N}_k \bar{\psi}_k\}_i - \{\sum \dot{N}_k \bar{\psi}_k\}_e - \dot{W}_{\text{cv}} - \dot{i}$$

$$-\dot{N}_{F,b}(\bar{u}_F - T_o \bar{s}_F) = \{\sum \dot{N}_k \hat{\psi}_k\}_i - \{\sum \dot{N}_k \hat{\psi}_k\}_e - \dot{W}_{cv} - \dot{I} \quad (D)$$

where the fuel burn rate $(dN_F/dt) = -\dot{N}_{F,b}$. Now

$$(\bar{u}_F - T_o \bar{s}_F) \approx \bar{h}_F - P \bar{v}_F - T_o \bar{s}_F = \bar{\psi}_F - P \bar{v} \quad (E)$$

Dividing Eq. (D) by the fuel burn rate,

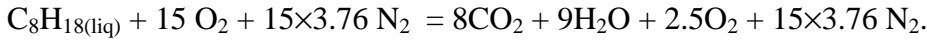
$$\begin{aligned} \bar{\psi}_F + (\sum (\dot{N}_k / \dot{N}_{F,b}) \hat{\psi}_k)_i - (\sum (\dot{N}_k / \dot{N}_{F,b}) \hat{\psi}_k)_e - (\dot{W} / \dot{N}_{F,b}) - (\dot{I} / \dot{N}_{F,b}) = 0, \text{ or} \\ \bar{\psi}_F + (\sum \bar{v}_k \hat{\psi}_k)_i - (\sum \bar{v}_k \hat{\psi}_k)_e - \bar{w} - \dot{i} - P \bar{v}_F = 0. \end{aligned} \quad (F)$$

$$\bar{w} = \bar{\Psi}_R - \bar{\Psi}_P - \dot{i} - P \bar{v}_F, \text{ where } \bar{\Psi}_R = \bar{\psi}_F + (\sum \bar{v}_k \hat{\psi}_k)_i, \bar{\Psi}_P = (\sum \bar{v}_k \hat{\psi}_k)_e.$$

Note that $\bar{\Psi}_R = \{\sum \dot{N}_k \hat{\psi}_k\}_i$ is the availability of air crossing the boundary of car. The optimum work

$$\bar{w}_{opt} = \bar{\Psi}_R - \bar{\Psi}_P - P \bar{v}_F.$$

The reaction equation that represents the complete combustion of a kmole of C_8H_{18} with 20% excess air is



At the inlet

$$\bar{\Psi}_R = (\bar{\psi}_F + \bar{v}_{O_2} \hat{\psi}_{O_2} + \bar{v}_{N_2} \hat{\psi}_{N_2})_i, \text{ where}$$

$$\bar{\psi}_F = \bar{h}_F - T_o \bar{s}_F = -249910 - 298 \times 360.79 = -357425 \text{ kJ per kmole of fuel.} \quad (G)$$

In case of air

$$X_{O_2} = 15 \div (15 + 15 \times 3.76) = 0.21, \text{ and}$$

$$\hat{\psi}_{O_2} = \bar{h}_{O_2} - T_o \bar{s}_{O_2}(T_o, p_{O_2}) = 0 - 298 \times (205.04 - 8.314 \times \ln(0.21 \times 1 \div 1)), \text{ i.e.,} \quad (G)$$

$$\hat{\psi}_{O_2} = -64969 \text{ kJ per kmole of } O_2.$$

Likewise,

$$X_{N_2} = 0.79, \text{ and } \hat{\psi}_{N_2} = -57651 \text{ kJ per kmole of } N_2.$$

Using Eqs. (E)–(G),

$$\begin{aligned} \bar{\Psi}_R = \bar{\psi}_F + (\sum \bar{v}_k \hat{\psi}_k)_i = (-357,425) + 15 \times (-64969) + 56.43 \times (-57,651) = \\ -4585118 \text{ per kmole of fuel burned.} \end{aligned}$$

$$\bar{\Psi}_P = (\bar{v}_{CO_2} \hat{\psi}_{CO_2} + \bar{v}_{H_2O} \hat{\psi}_{H_2O} + \bar{v}_{O_2} \hat{\psi}_{O_2} + (\bar{v}_{N_2} \hat{\psi}_{N_2}))_e, \text{ where} \quad (H)$$

$$X_{CO_2} = 8 \div (8 + 9 + 2.5 + 56.43) = 0.1053 \text{ and } p_{CO_2} = 0.1053 \times 1 = 0.1053 \text{ bar,}$$

$$\text{Similarly, } X_{H_2O} = 0.1185, X_{O_2} = 0.0329, X_{N_2} = 0.7432.$$

We can now determine the values of the $\hat{\psi}_{k,e}$'s, e.g.,

$$\hat{\psi}_{\text{CO}_2} = (-393520 + 13372 - 9364) - 298 \times 225.225 = -456,629 \text{ kJ (kmole CO}_2\text{)}^{-1}. \quad (\text{I})$$

Hence,

$$\bar{\Psi}_P = (\sum \bar{v}_k \hat{\psi}_k)_e = -9835835 \text{ kJ per kmole of fuel burnt, and} \quad (\text{J})$$

$\bar{w}_{\text{opt}} = (-4585118 - (-9835835)) - 100 \times 114 \div 703 = 5250700 \text{ kJ per kmole of burned fuel, or}$

$$122569 \text{ kJ gallon}^{-1} \text{ assuming the liquid density to be } 703 \text{ kg m}^{-3}.$$

Remarks

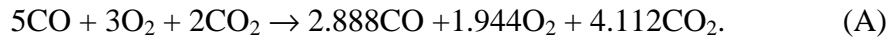
The work that can be developed by a 20 gallon (1 gallon = 3.7854 l) tank of octane is 2451374 kJ. Since 1 kW hr = 3600 kJ, in the case of this example $W_{\text{opt}} = 681 \text{ kW hr}$, and an automobile with a power output of 100 kW (a 6 cylinder engine) can be ideally drive for 6.81 hrs and at 50 kW can drive for 13.62 hrs. At a speed of 60 mph for a 6 cylinder car this allows the vehicle to cover a distance of 409 miles at a maximum of 20.5 miles per gallon for 100 kW engine and 41 MPH for 50 kW engine. The typical work output of an automobile is roughly $42500 \text{ kJ gallon}^{-1}$ due to nonideal conditions.

Example 4

Five kmole of CO, three kmole of O₂, and two kmole of CO₂ are fully mixed when they enter a combustor at 3000 K and 1 bar. The products leave the combustor at the same temperature and pressure at equilibrium. Determine the optimum work.

Solution

The equilibrium composition for this problem is readily determined using similar procedure given in Example 7 of Chapter 12. The overall reaction can thereafter be represented by the equation



$$W_{\text{opt}} = \text{availability in} - \text{availability out} = \Psi_R - \Psi_P, \text{ where} \quad (\text{B})$$

$$\Psi_R = (5\hat{\psi}_{\text{CO}} + 3\hat{\psi}_{\text{O}_2} + 2\hat{\psi}_{\text{CO}_2})_i, \text{ and} \quad (\text{C})$$

$$\Psi_P = (2.888\hat{\psi}_{\text{CO}} + 1.944\hat{\psi}_{\text{O}_2} + 4.112\hat{\psi}_{\text{CO}_2})_e. \quad (\text{D})$$

Now,

$$\begin{aligned} \hat{\psi}_{\text{CO},i} &= \bar{h}_{\text{CO}}(T,p_{\text{CO}}) - T_o \bar{s}_{\text{CO}} = \bar{g}_{\text{CO}} + (T - T_o) \bar{s}_{\text{CO}} = \\ &= (-110530) + 96395.7 - 298 \times (274.6 - 8.314 \times \ln((5 \div (5+3+2)) \times 1)) = \\ &= (-0.9772 \times 10^5) \text{ kJ per kmole of CO,} \end{aligned}$$

$$\begin{aligned} \hat{\psi}_{\text{O}_2,i} &= 0 + 98152.9 - 298 \times (284.4 - 8.314 \times \ln((3 \div 10) \times 1)) = \\ &= 0.1042 \times 10^5 \text{ kJ per kmole of O}_2, \text{ and} \end{aligned}$$

$$\begin{aligned} \hat{\psi}_{\text{CO}_2,i} &= -393520 + 152347.9 - 298 \times (332.9 - 8.314 \times \ln 0.2) = \\ &= (-0.3444 \times 10^6) \text{ kJ per kmole of CO}_2. \end{aligned}$$

Therefore,

$$\Psi_R = -1.146 \times 10^6 \text{ kJ} \quad (\text{E})$$

At the exit (in units of kJ),

$$\hat{\psi}_{\text{CO},e} = -0.9866 \times 10^5, \hat{\psi}_{\text{O}_2,e} = 9699.5, \text{ and } \hat{\psi}_{\text{CO}_2,e} = -0.3424 \times 10^6 \text{ kJ, i.e.,}$$

$$\Psi_P = -1.6215 \times 10^6 \text{ kJ} \quad (\text{F})$$

Hence,

$$W_{\text{opt}} = (-1.146 + 1.6215) \times 10^6 = 475500 \text{ kJ per 5 kmole of CO consumed} \quad (\text{G})$$

or 95100 kJ per kmole of CO entering the reactor..

This is an example of isothermal availability since $T_{\text{react}} = T_{\text{prod}}$

Example 5

Consider the adiabatic and stoichiometric combustion of molecular hydrogen with air. The inlet conditions to the burner are at 298 K and 1 bar (state 1). The products leave the combustor at state 2. Determine the irreversibility. If the products are cooled back to 298 K (state 3), determine the optimum work. Assume that H₂O exists as a gas at 298 K.

Solution

The overall chemical reaction is



Recall that $\sigma = W_{\text{opt}}/T_o$, where

$$W_{\text{opt}} = \Psi_1 - \Psi_2.$$

With the values

$$X_{\text{H}_2} = 1/(1+0.5+1.88) = 0.296, X_{\text{O}_2} = 0.148, X_{\text{N}_2} = 0.556,$$

$$\Psi_1 = N_{\text{H}_2} \hat{\psi}_{\text{H}_2} + N_{\text{O}_2} \hat{\psi}_{\text{O}_2} + N_{\text{N}_2} \hat{\psi}_{\text{N}_2}, \text{ where, for instance}$$

$$\hat{\psi}_{\text{H}_2} = \bar{h}_{\text{H}_2}(T, p_{\text{H}_2}) - T_o \bar{s}_{\text{H}_2} \text{ and } p_{\text{H}_2} = X_{\text{H}_2} P,$$

$$\begin{aligned} \Psi_1 = & (0 - 298 \times (130.57 - 8.314 \times \ln(1 \times 0.296/1))) + \\ & 1/2 \times (0 - 298 \times (205.03 - 8.314 \times \ln(1 \times 0.148/1))) + \\ & 1.88 \times (0 - 209 \times (191.5 - 8.314 \times \ln(1 \times 0.556/1))) = -184920 \text{ kJ} \end{aligned}$$

The adiabatic flame temperature is obtained by considering the energy balance

$$dE_{\text{cv}}/dt = \dot{Q}_{\text{cv}} - \dot{W}_{\text{cv}} + \sum_{k,i} \dot{N}_k \bar{e}_{T,k} - \sum_{k,e} \dot{N}_k \bar{e}_{T,k}$$

Under ideal gas conditions $\hat{h}_k = \bar{h}_k$, and assuming negligible contributions from the potential and kinetic energies, steady state, and a single step overall chemical reaction, and in the absence of work

$$(\sum \bar{v}_k \bar{h}_{T,k})_i = (\sum \bar{v}_k \bar{h}_{T,k})_e, \text{ or } H_1 = H_2, \text{ where}$$

$$H_1 = \bar{v}_{\text{H}_2,i} \bar{h}_{\text{H}_2,i} + \bar{v}_{\text{O}_2,i} \bar{h}_{\text{O}_2,i} + \bar{v}_{\text{N}_2,i} \bar{h}_{\text{N}_2,i} = 0 \text{ (elemental species), and}$$

$$H_1 = \bar{v}_{\text{O}_2,e} \bar{h}_{\text{O}_2,e} + \bar{v}_{\text{N}_2,e} \bar{h}_{\text{N}_2,e} + \bar{v}_{\text{H}_2\text{O},e} \bar{h}_{\text{H}_2\text{O},e} = 0.$$

Solving iteratively, $T_2 = T_{\text{ad}} = 2528.7 \text{ K}$.

$$\Psi_2 = N_{\text{H}_2\text{O},e} \hat{\psi}_{\text{H}_2\text{O},e} + N_{\text{O}_2,e} \hat{\psi}_{\text{O}_2,e} + N_{\text{N}_2,e} \hat{\psi}_{\text{N}_2,e}, \text{ i.e.,}$$

$$\begin{aligned} \Psi_2 = & 1 \times (-241820 + 99704 - 298 \times (276.4 - 8.314 \times \ln(1 \times 0.347/1))) + \\ & 0 + 1.88 (0 + 75597 - 298 \times (260.7 - 8.314 \times \ln(1 \times 0.653/1))) = \\ & (-233079) \text{ kJ.} \end{aligned}$$

$$W_{\text{opt},12} = -184920 - (-233079) = 48159 \text{ kJ per kmole of fuel burnt.}$$

$$\dot{i}_{12} = 48159 \text{ kJ per kmole of fuel.}$$

$$\bar{\sigma}_{12} = 48159 \div 298 = 162 \text{ kJ K}^{-1} \text{ per kmole of fuel.}$$

If the gases are cooled from $T_2 = 2528.7$ to $T_3 = T_0 = 298 \text{ K}$, but with the same composition,

$$W_{\text{opt},23} = \Psi_2 - \Psi_3, \text{ where}$$

$$\begin{aligned} \Psi_3 &= 1 \times (-241820 + 298 \times (188.72 - 8.314 \times \ln(1 \times 0.347 \div 1))) + \\ & 0 + 1.88 \times (0 - 298 \times (191.5 - 8.314 \times \ln(1 \times 0.653 \div 1))) = \\ & (-408259) \text{ kJ per kmole of fuel, i.e.,} \end{aligned}$$

$$W_{\text{opt},23} = -233079 - (-408259) = 175180 \text{ kJ per kmole of fuel.}$$

Remarks

1. The stream exergy at state 1 is $\Psi_1 - \Psi_0 = \Psi_1 - \Psi_3 = W_{\text{opt},13} = -184,920 - (-408259) = 223,339 \text{ kJ}$; Even though state 2 has same enthalpy as state 1, the stream exergy at state 2 is $\Psi_2 - \Psi_0 = \Psi_2 - \Psi_3 = W_{\text{opt},23} = 175,180$. Thus defining availability fraction at state 2 as $\xi_{\text{opt},23} = W_{\text{opt},23} / W_{\text{opt},13} = 0.78$ which indicates that approximately 22 % of maximum possible optimum work which was otherwise available at state 1 is lost during the irreversible adiabatic combustion.

1. One can repeat calculations for a stoichiometric mixture of methane and air entering the burner at 298 K and 1 atm; then the flame temperature, optimum work and availability fraction at the flame temperature are given as $T_{\text{ad}} = 2325 \text{ K}$, $W_{\text{loss}} = 236 \text{ MJ/kmol}$, and $\xi_{\text{opt},23} = 0.72$ (i.e. availability loss fraction of 0.28). The temperature of 2325 K is achieved when the combustion proceeds without any loss of heat to the surroundings [$H(\text{products}) - H(\text{reactants})$]. The only irreversibility is the chemical reaction. We see, therefore, that a combustion reaction is highly irreversible and wasteful of availability, even when it is conducted so that enthalpy of combustion is retained in the combustion products. In this instance, 28% of the initial availability is lost. Availability analysis reveals that chemical processes may be degrading energy quality while conserving quantity.

Example 6

The stoichiometric combustion of molecular hydrogen in air proceeds in a premixed state. The reactants enter a combustor at 298 K and 1 bar and the products leave at the same temperature and pressure. Determine the values of σ and Δh_c if the water formed exists in a liquid or in a gaseous state..

Solution

The overall chemical reaction is



Recall that $\sigma = W_{\text{opt}}/T_0$, where

$$\bar{w}_{\text{opt}} = \Psi_1 - \Psi_2.$$

With the values

$$X_{\text{H}_2} = 1 \div (1 + 0.5 + 1.88) = 0.296, X_{\text{O}_2} = 0.148, X_{\text{N}_2} = 0.556,$$

$$\hat{g}_{\text{H}_2} = (0 - 298 \times (130.57 - 8.314 \times \ln(1 \times 0.296 \div 1))) = -41926 \text{ kJ kmole}^{-1},$$

$$\hat{g}_{\text{O}_2} = 0 - 298 \times (205.03 - 8.314 \times \ln(1 \times 0.148 \div 1)) = -65832 \text{ kJ kmole}^{-1},$$

$$\hat{g}_{\text{N}_2} = -298 \times (191.5 - 8.314 \times \ln(1 \times 0.556 \div 1)) = -58521 \text{ kJ kmole}^{-1},$$

$$\Psi_1 = G_1 = (-41,926) + 1/2 \times (-65,832) + 1.88 \times (-58,521) = -184861 \text{ kJ per kmole of H}_2.$$

Treating H₂O as a gas,

$$X_{\text{H}_2\text{O}} = 1 \div (1 + 1.88) = 0.347, X_{\text{N}_2} = 0.653,$$

$$\hat{g}_{\text{H}_2\text{O}} = -241820 - 298 \times (188.71 - 8.314 \times \ln(1 \times 0.347/1)) = -300678 \text{ kJ kmole}^{-1},$$

$$\hat{g}_{\text{N}_2} = -298 \times (191.5 - 8.314 \times \ln(1 \times 0.653/1)) = -58123 \text{ kJ kmole}^{-1},$$

$$\Psi_2 = G_2 = (-300678) + 1.88 \times (-58123) = -4100392 \text{ kJ per kmole of H}_2,$$

$$\bar{w}_{\text{opt}} = -184861 - (-4100392) = 22178 \text{ kJ per kmole of H}_2.$$

All of this work is lost. Therefore,

$$\bar{\sigma} = 225090 \div 298 = 755.34 \text{ kJ kmole}^{-1} \text{ K, and}$$

$$\Delta h_c = 0 + -(-241820) = 241820 \text{ kJ per kmole of H}_2.$$

Treating H₂O as a liquid,

$$\hat{g}_{\text{H}_2\text{O}} = \bar{g}_{\text{H}_2\text{O}} = -285830 - 298 \times 69.95 = -306675 \text{ kJ per kmole of H}_2,$$

$$\Psi_2 = 1 \times 1 (-285830 - 298 \times (69.95)) + 1.88 (0 - 298 \times (191.5 - 8.314 \times \ln(1 \times 1 \div 1))) = (-413961) \text{ kJ per kmole of H}_2, \text{ and}$$

$$\bar{w}_{\text{opt}} = 229098 \text{ kJ per kmole of H}_2.$$

Consequently,

$$\bar{\sigma} = 229098 \div 298 = 768.8 \text{ kJ kmole}^{-1}, \text{ and}$$

$$\Delta h_c = 285830 \text{ kJ per kmole of H}_2.$$

Example 7

Find the maximum work deliverable in a fuel cell by 1 kmole of H₂ with O₂ if it is isothermally reacted at 25°C and 1 bar to produce liquid water. Both reactants enter the cell separately. Determine the maximum voltage developed by the fuel cell. Consider also the scenario for the reaction of a stoichiometric amount of H₂ with O₂. What is maximum possible fuel cell efficiency. Assume that $\Delta h_c = 285830 \text{ kJ kmole}^{-1}$.

Solution

The fuel cell temperature $T = T_o = 25^\circ\text{C}$, and the two reactant streams enter separately. Consequently,

$$\dot{W}_{\text{opt}} = (\sum_k \dot{N}_k \bar{g}_k)_i - (\sum \dot{N}_k \bar{g}_k)_e.$$

Assume that $\dot{N}_{\text{H}_2} = 1 \text{ kmole s}^{-1}$. In that case, $\dot{N}_{\text{O}_2} = 1/2 \text{ kmole s}^{-1}$, and $\dot{N}_{\text{H}_2\text{O}} = 1 \text{ kmole s}^{-1}$, and

$$(\sum \dot{N}_k \bar{g}_k)_i = \bar{g}_{\text{H}_2} + (1/2) \bar{g}_{\text{O}_2}, \text{ where}$$

$$\bar{g}_{\text{H}_2} = 0 - 298 \times 130.574 = -38911 \text{ kJ kmole}^{-1}, \text{ and}$$

$$\bar{g}_{\text{O}_2} = 0 - 298 \times 205.033 = -61100 \text{ kJ kmole}^{-1}, \text{ i.e.,}$$

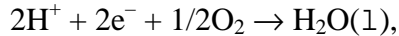
$$(\sum \dot{N}_k \bar{g}_k)_i = -69461 \text{ kJ per kmole of H}_2.$$

Likewise,

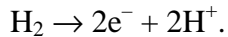
$$(\sum \dot{N}_k \bar{g}_k)_e = -306675 \text{ kJ per kmole of H}_2, \text{ so that}$$

$$\bar{w}_{\text{opt}} = G_{\text{reactants}} - G_{\text{products}} = -69461 + 306675 = 237214 \text{ kJ per kmole of H}_2.$$

At the anode of a fuel cell positive potential is applied according to the reaction



and at the cathode the pertinent reaction is



Overall, a molecule of H_2 generates 2 electrons and mole of the substance, i.e., 6.023×10^{26} molecules generates $2 \times 6.023 \times 10^{26}$ electrons. An electron carries a charge of 1.602×10^{-19} Coulomb so that a kmole of H_2 generates a charge of $1.602 \times 10^{-19} \times 2 \times 6.023 \times 10^{26}$ Coulomb.

The electrical work

$$\begin{aligned} W_{\text{elec}} &= \text{Voltage in volts} \times \text{charge in coulombs} = \\ &237214 \text{ kJ per kmole of } \text{H}_2 \times 1000 \text{ J kJ}^{-1} \div \\ &(1.602 \times 10^{-19} \times 2 \times 6.023 \times 10^{26} \text{ Coulomb}) = \\ &1.229 \text{ V.} \end{aligned}$$

In case the mixture is premixed, the partial pressures of H_2 and O_2 must be accounted for. In this case

$$\bar{w}_{\text{opt}} = 229334 \text{ kJ per kmole of } \text{H}_2, \text{ and } V = 1.187 \text{ V.}$$

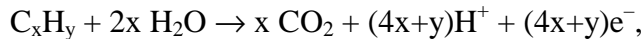
The optimum fuel cell efficiency

$$(\eta_{\text{fc}})_{\text{opt}} = \bar{w}_{\text{opt}} / \Delta h_{\text{c}} = 237214 / 285830 = 0.83.$$

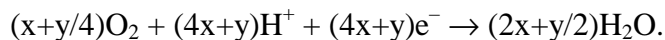
Remarks

A short formula for determining the voltage of a fuel cell is Volts = $(\Delta G$ per kmole of fuel in kJ) $\times 1.036 \times 10^{-5} \div$ (Number of electrons generated per molecule of the fuel). Fuel cells may be connected in series to obtain a higher voltage than an individual cell provides.

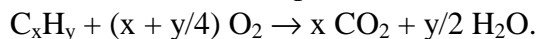
For fuel cells using hydrocarbon fuels, the anodic reaction is



and the cathodic reaction is



The overall reaction can be represented as



Therefore, for a hydrocarbon fuel C_xH_y , the electrons generated per molecule are represented by the relation $(4x+y)$.

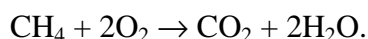
In the context of H_2 example, had we supplied work or applied an emf of 1.23 V, the reaction could have been reversed to produce H_2 and O_2 from H_2O . In this case, water that is formed from the hydrogen and oxygen could be converted back into the respective fuels through a reversible process so that $\sigma = 0$.

Example 8

Determine the fuel availability for methane. Assume that $T_o = 298 \text{ K}$, $p_{\text{O}_2,o} = 0.2055$, $p_{\text{CO}_2,o} = 0.003$, and $p_{\text{H}_2\text{O},o} = 0.0188$. If the lower heating value LHV of methane is $802330 \text{ kJ kmole}^{-1}$, determine the ratio of the fuel availability to LHV.

Solution

Consider the overall reaction



The fuel availability

$$\text{Avail}_F = \bar{w}_{\text{opt}} = \Psi_R - \Psi_{P,\text{TMC}}$$

$$\Psi_R = (\bar{\psi}_{\text{CH}_4}(T_o, P_o) + 2\bar{\psi}_{\text{O}_2}(T_o, p_{\text{O}_2, o})), \text{ where}$$

$$\bar{\psi}_{\text{CH}_4}(T_o, P_o) = \bar{h}_{\text{CH}_4} - T_o \bar{s}_{\text{CH}_4}(T_o, P_o) = -74850 - 298 \times 186.16 =$$

$$(-1.303 \times 10^5) \text{ kJ kmole}^{-1},$$

$$\bar{\psi}_{\text{O}_2}(T_o, p_{\text{O}_2, o}) = \bar{h}_{\text{O}_2} - T_o \bar{s}_{\text{O}_2}(T_o, p_{\text{O}_2, o}) =$$

$$0 - 298 \times (205.04 - 8.314 \times \ln(0.2055 \div 1)) =$$

$$(-65022) \text{ kJ kmole}^{-1}, \text{ i.e.,}$$

$$\Psi_R = 1 \times (-130300) + 2 \times (-65022) = -260300 \text{ kJ per kmole of CH}_4.$$

Likewise,

$$\bar{\psi}_{\text{CO}_2} = \bar{h}_{\text{CO}_2} - T_o \bar{s}_{\text{CO}_2}(T_o, p_{\text{CO}_2, \infty}) =$$

$$(-393520 - 298 \times (213.7 - 8.314 \times \ln(0.003 \div 1))) =$$

$$(-472000) \text{ kJ per kmole of CO}_2,$$

$$\bar{\psi}_{\text{H}_2\text{O}} = \bar{h}_{\text{H}_2\text{O}} - T_o \bar{s}_{\text{H}_2\text{O}}(T_o, p_{\text{H}_2\text{O}, \infty}) =$$

$$(-241820) - 298 \times (188.7 - 8.314 \times \ln(0.0188 \div 1)) =$$

$$-307900 \text{ kJ per kmole of H}_2\text{O, i.e.,}$$

$$\Psi_{P,\text{TMC}} = 1 \times (-472000) + 2 \times (-307900) = -1088000 \text{ kJ per kmole of fuel.}$$

Therefore,

$$\text{Avail}_F = -260300 - (-1088000) = 827500 \text{ kJ per kmole of fuel.}$$

The ratio

$$\text{Avail}_F/\text{LHV} = 827500 \div 802330 = 1.031.$$

Remarks

This procedure can be repeated for butane, for which $\text{Avail}_F = 2767296$ kJ per kmole of fuel and the ratio $\text{Avail}_F/\text{LHV} = 2767296 \div 2708330 = 1.0218$. For most hydrocarbon fuels, the ratio of fuel availability to the lower heating value is in the range 1.02–1.07.

An empirical relation for [Moran]

$$\text{Avail}_F/\text{LHV} = 1.033 + 0.0169 \{H/C\} - 0.0698/C, \text{ gaseous hydrocarbon,}$$

C: carbon atom, H: hydrogen atom and

$$\text{Avail}_F/\text{LHV} = 1.0422 + 0.0119 \{H/C\} - 0.042/C, \text{ liquid HC}$$