

1.1

A mixture of one mole of gaseous ethene and three moles of oxygen at 298 K react in a constant volume bomb. Heat is transferred until the products are cooled to 600 K. Determine the amount of heat released in cal/gm-mole of the fuel. Assume no dissociation of products.

The chemical reaction is



The first law for reacting systems is:

$$\Delta Q + U_R = U_P$$

where the " U_R " is internal energy of reactants and " U_P " is the internal energy of products, since it is a constant volume process.

$$\Delta Q + \sum_R n(\Delta h_f^\circ + \int_{T_0}^T c_p dT - R_u T) = \sum_P n(\Delta h_f^\circ + \int_{T_0}^T c_p dT - R_u T)$$

$$\sum_R n(\Delta h_f^\circ + \int_{T_0}^T c_p dT - R_u T) = (\Delta h_f^\circ - R_u T)_{\text{C}_2\text{H}_4} - n_{\text{O}_2} (R_u T)_{\text{O}_2} = (\Delta h_f^\circ)_{\text{C}_2\text{H}_4} - 4 R_u T$$

$$= 12,540 - 4 \times 1.987 \times 298 = 10,171 \text{ cal/gm-mole of fuel}$$

$$\sum_P n(\Delta h_f^\circ + \int_{T_0}^T c_p dT - R_u T) = 2(\Delta h_f^\circ)_{\text{CO}_2} + 2\Delta h_{\text{CO}_2} + 2(\Delta h_f^\circ)_{\text{H}_2\text{O}} + 2\Delta h_{\text{H}_2\text{O}(g)} - 4 R_u T$$

$$= 2(-94054 + 3084) + 2(-57798 + 2515) - 4 \times 1.987 \times 600$$

$$= -181940 - 110566 - 4769 = -297275 \text{ cal/gm-mole of fuel}$$

Therefore ,

$$\Delta Q = -297,275 - 10,171 = -307,446 \text{ cal/gm-mole fuel}$$

This analysis assumed negligible changes in kinetic and potential energy.

1. 2

We have already considered the first law of thermodynamics for a system, which consists of a fixed quantity of mass, and noted, Eq. (1-24), that it may be written

$${}_1\hat{Q}_2 = E_2 - E_1 + {}_1\hat{W}_2$$

We have also noted that this may be written as an average rate equation, over the time interval δt by dividing by δt

$$\frac{\delta \hat{Q}}{\delta t} = \frac{E_2 - E_1}{\delta t} + \frac{\delta \hat{W}}{\delta t} \quad (1)$$

In order to write the first law as a rate equation for a control volume, we define a system and a control volume shown in the following figure. The system consists of all the mass initially in the control volume plus the mass δm_i .

Consider the changes that take place in the system and control volume during the time interval δt . During this time δt the mass δm_i enters the control volume through the discrete area A_i , and the mass δm_e leaves the control volume through the area A_e .

In our analysis we will assume that the increment of mass, δm_i has uniform properties, and similarly that δm_e has uniform properties.

The total work done by the system during this process, $\delta \hat{W}$, is that associated with the masses δm_i and δm_e crossing the control surface, usually referred to as flow work, and the work $\delta \hat{W}_{c.v.}$ which includes all other forms of work, such as work associated with a rotating shaft that crosses the

system boundary, shear forces, electrical, magnetic or surface effects, or expansion or contraction of the control volume. An amount of heat $\delta\hat{Q}$ crosses the boundary during δt .

Let us now consider each of the terms of the first law as it is written for the system, and transform each term into an equivalent form that applies to the control volume. Consider first the term $E_2 - E_1$.

Let E_t = the energy in the control volume at time t , $E_{t+\delta t}$ = the energy in the control volume at time $t+\delta t$.

Then

$$E_1 = E_t + e_i \delta m_i = \text{energy of the system at time } t$$

$$E_2 = E_{t+\delta t} + e_e \delta m_e = \text{energy of the system at time } t+\delta t.$$

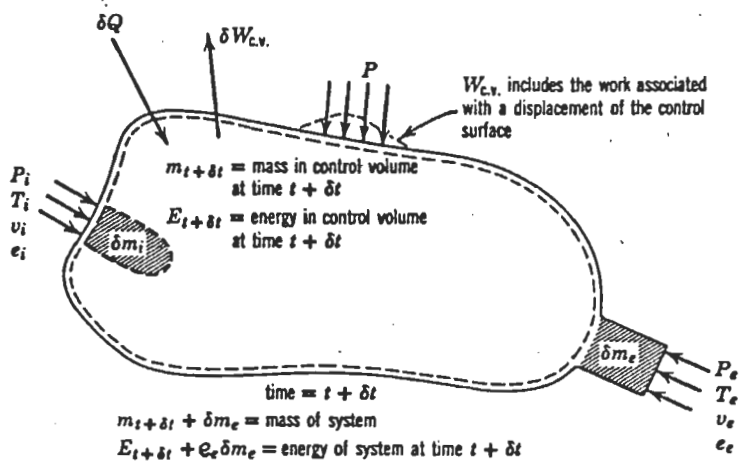
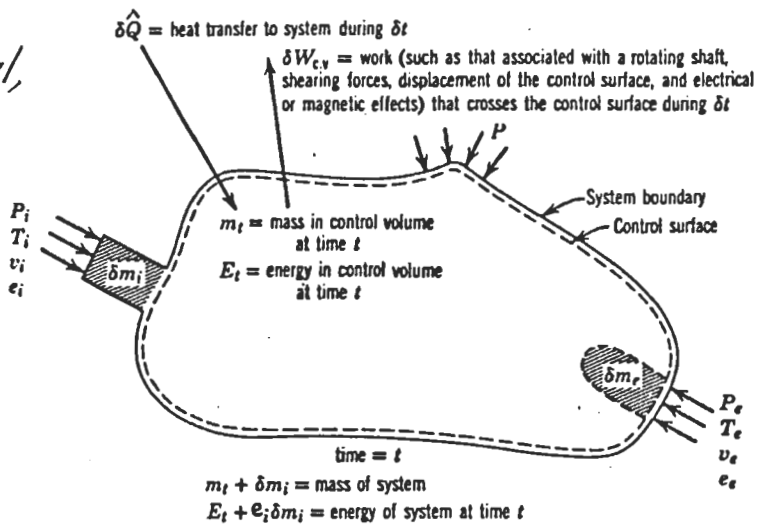
Therefore

$$E_2 - E_1 = E_{t+\delta t} + e_e \delta m_e - E_t - e_i \delta m_i$$

$$= (E_{t+\delta t} - E_t) + (e_e \delta m_e - e_i \delta m_i) \quad (2)$$

The term $(e_e \delta m_e - e_i \delta m_i)$ represents the net flow of energy that crosses the control surface during δt as the result of the masses δm_e and δm_i crossing the control surface.

Let us consider in more detail the work associated



Schematic diagram for a first law analysis of a control volume, showing heat and work as well as mass crossing the control surface.

with the masses δm_i and δm_e crossing the control surface. Work is done by the normal force (normal to area \mathcal{A}) acting on δm_i and δm_e as these masses cross the control surface. This normal force is equal to the product of the normal tensile stress, $-\sigma_n$, and the area, \mathcal{A} . The work done is

$$-\sigma_n \mathcal{A} d\ell = -\sigma_n \delta V = -\sigma_n v \delta m \quad (3)$$

A complete analysis of the nature of the normal stress, σ_n , for an actual fluid involves both static pressure and viscous effects, and is beyond the scope of this Chapter. We will assume in this Chapter that the normal stress, σ_n , at a point is equal to the static pressure at this point, P , and simply note that in many applications this is a very reasonable assumption and yields results of good accuracy.

With this assumption the work done on mass δm_i as it enters the control volume is $P_i v_i \delta m_i$, and the work done by mass δm_e as it leaves the control volume is $P_e v_e \delta m_e$. We shall refer to these terms as the flow work. Various other terms are encountered in the literature such as flow energy and work of introduction and work of expulsion.

Thus the total work done by the system during time δt is

$$\delta \hat{W} = \delta \hat{W}_{c.v.} + \underbrace{[P_e v_e \delta m_e - P_i v_i \delta m_i]}_{\text{flow work}} \quad (4)$$

Let us now divide Eqs. (2) and (4) by δt and substitute into the first law, Eq. (1). Combining terms and rearranging,

$$\frac{\delta \hat{Q}}{\delta t} + \frac{\delta m_i}{\delta t} (e_i + P_i v_i) = \left(\frac{E_{t+\delta t} - E_t}{\delta t} \right) + \frac{\delta m_e}{\delta t} (e_e + P_e v_e) + \frac{\delta \hat{W}_{c.v.}}{\delta t} \quad (5)$$

We recognize that each of the flow terms in this expression can be rewritten in the form

$$\begin{aligned} e + P v &= u + P v + \frac{V^2}{2g_c} + Z \frac{g}{g_c} \\ &= h + \frac{V^2}{2g_c} + Z \frac{g}{g_c} \end{aligned} \quad (6)$$

using the definition of the thermodynamic property enthalpy, Eq. (1-70). It should be apparent that the appearance of the combination $(u + Pv)$ whenever mass flows across a control surface is the principal reason for defining the property enthalpy. Its introduction earlier in conjunction with the constant-pressure process was to facilitate use of the tables of thermodynamic properties at that time.

Utilizing Eq. (6) for the masses entering and leaving the control volume, Eq. (5) becomes

$$\frac{\delta \hat{Q}}{\delta t} + \frac{\delta m_i}{\delta t} \left(h_i + \frac{V_i^2}{2g_c} + Z_i \frac{g}{g_c} \right) = \left(\frac{E_{t+\delta t} - E_t}{\delta t} \right) + \frac{\delta m_e}{\delta t} \left(h_e + \frac{V_e^2}{2g_c} + Z_e \frac{g}{g_c} \right) + \frac{\delta \hat{W}_{c.v.}}{\delta t} \quad (7)$$

In order to reduce this expression to a rate equation, let us now examine each of the terms and establish the limits as δt is made to approach zero.

As regards the heat transfer, as δt approaches zero the system and the control volume coincide, and the heat transfer rate to the system is also the heat transfer rate to the control volume.

Therefore, $\lim_{\delta t \rightarrow 0} \frac{\delta \hat{Q}}{\delta t} = \dot{Q}_{c.v.}$

the rate of heat transfer to the control volume.

Further

$$\lim_{\delta t \rightarrow 0} \left(\frac{E_{t+\delta t} - E_t}{\delta t} \right) = \frac{dE_{c.v.}}{dt}$$

$$\lim_{\delta t \rightarrow 0} \left(\frac{\delta \hat{W}_{c.v.}}{\delta t} \right) = \dot{W}_{c.v.}$$

$$\lim_{\delta t \rightarrow 0} \left(\frac{\delta m_i}{\delta t} \left(h_i + \frac{V_i^2}{2g_c} + Z_i \frac{g}{g_c} \right) \right) = \dot{m}_i \left(h_i + \frac{V_i^2}{2g_c} + Z_i \frac{g}{g_c} \right)$$

$$\lim_{\delta t \rightarrow 0} \left(\frac{\delta m_e}{\delta t} \left(h_e + \frac{V_e^2}{2g_c} + Z_e \frac{g}{g_c} \right) \right) = \dot{m}_e \left(h_e + \frac{V_e^2}{2g_c} + Z_e \frac{g}{g_c} \right)$$

We originally assumed uniform properties for the incremental mass δm_i entering the control volume across area A_i , and made a similar assumption for δm_e leaving across area A_e . Consequently, in taking the limits above, this reduces to the restriction of uniform properties across area A_i and also A_e at an instant of time. These may of course be time dependent.

In utilizing these limiting values to express the rate equation of the first law for a control volume, we again include summation signs on the flow terms to account for the possibility of

additional flow streams entering or leaving the control volume. Therefore, the result is

$$\dot{Q}_{c.v.} + \sum \dot{m}_i \left(h_i + \frac{V_i^2}{2g_c} + z_i \frac{g}{g_c} \right) = \frac{dE_{c.v.}}{dt} + \sum \dot{m}_e \left(h_e + \frac{V_e^2}{2g_c} + z_e \frac{g}{g_c} \right) + \dot{W}_{c.v.} \quad (8)$$

which is, for our purposes, the general expression of the first law of thermodynamics. In words, this equation says that the rate of heat transfer into the control volume plus rate of energy flowing in as a result of mass transfer is equal to the rate of change of energy inside the control volume plus rate of energy flowing out as a result of mass transfer plus the power output associated with shaft, shear, and electrical effects and other factors that have already been mentioned.

Equation (8) can be integrated over the total time of a process to give the total energy changes that occur during that period. However, to do so requires knowledge of the time dependency of the various mass flow rates and the states at which mass enters and leaves the control volume.

1.3

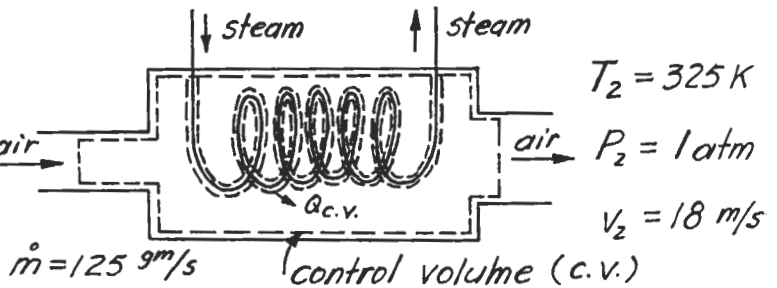
Given :

$$C_{p,air} = 0.24 \frac{\text{cal}}{\text{gm} \cdot \text{K}}$$

$$T_1 = 290 \text{ K}$$

$$P_1 = 1.2 \text{ atm}$$

$$V_1 = 15 \text{ m/s}$$



$$T_2 = 325 \text{ K}$$

$$P_2 = 1 \text{ atm}$$

$$V_2 = 18 \text{ m/s}$$

From problem 2, we have

$$\dot{Q}_{c.v.} + \dot{m} \left(h_1 + \frac{V_1^2}{2g_c} + g \frac{z_1}{g_c} \right) = \frac{dE_{c.v.}}{dt} + \dot{m} \left(h_2 + \frac{V_2^2}{2g_c} + g \frac{z_2}{g_c} \right) + \dot{W}_{c.v.}$$

\therefore steady state

given in problem statement

\therefore steady flow

$$\text{Note } \dot{m}_{in} = \dot{m}_{out} = \dot{m}$$

After rearranging, we have

$$\begin{aligned}
 \dot{Q}_{c.v} &= \dot{m} \left\{ (h_2 - h_1) + \frac{|V_2|^2 - |V_1|^2}{2g_c} \right\} \\
 &= 125 \frac{gm}{s} \left\{ 0.24 \frac{cal}{gm K} (325 - 290) K + \frac{1800^2}{2} \frac{cm^2}{s^2} \frac{1}{980.65 \frac{gm-cm}{gf-s^2}} \frac{cal}{gf-cm} \right. \\
 &\quad \left. - \frac{1500^2}{2} \frac{1}{980.65} \frac{1}{42664.9} \right\} \\
 &= 125 \frac{gm}{s} \left\{ 8.4 + (0.03872 - 0.02689) \right\} \frac{cal}{gm} \\
 &= 1051.5 \text{ cal/s} \\
 &= 4401.3 \text{ Joules/s}
 \end{aligned}$$

Note :

$$\begin{aligned}
 g_c &= 32.174 \frac{ft-lb_m}{lb_f-s^2} = 1 \frac{gm}{dyne} \frac{cm}{s^2} = 1 \frac{kg_m m}{N-s^2} \\
 &= 1 \frac{slug}{lb_f} \frac{ft}{s^2} = 980.65 \frac{gm cm}{gf-s^2} \\
 1 \text{ cal} &= 4.18585 \text{ Joules}
 \end{aligned}$$

1.4

The condition for chemical equilibrium at constant T and P is $\sum \mu_i dn_i = 0$ which includes the all components and phases. If the total number of species in this equilibrium reaction is N ; some of them have three phases (species 1... L), some of them have 2 phases (species $L+1$... $L+M$), and the rest of them only have one phase ($L+M+1$, ... N).

Then the equilibrium condition becomes

$$\begin{aligned}
 &\left. \begin{aligned}
 &\mu_1(l) dn_1(l) + \mu_1(g) dn_1(g) + \mu_1(s) dn_1(s) \\
 &+ \mu_2(l) dn_2(l) + \mu_2(g) dn_2(g) + \mu_2(s) dn_2(s) \\
 &\vdots \\
 &+ \mu_L(l) dn_L(l) + \mu_L(g) dn_L(g) + \mu_L(s) dn_L(s)
 \end{aligned} \right\} \begin{array}{l} \text{3 phases} \\ \text{(say, l.g.s)} \end{array} \\
 &+ \left. \begin{aligned}
 &\mu_{L+1}(l) dn_{L+1}(l) + \mu_{L+1}(g) dn_{L+1}(g) \\
 &\vdots \\
 &+ \mu_{L+M}(l) dn_{L+M}(l) + \mu_{L+M}(g) dn_{L+M}(g) \\
 &+ \mu_{L+M+1} dn_{L+M+1} + \dots + \mu_N dn_N = 0
 \end{aligned} \right\} \begin{array}{l} \text{2 phases} \\ \text{(say, l.g)} \\ \text{(1)} \end{array}
 \end{aligned}$$

In a closed chemical equilibrium system, the mass (mole) of every component is constant, that is

$$\begin{aligned}
 dn_1(\ell) + dn_1(g) + dn_1(s) &= 0 \\
 \vdots & \\
 dn_L(\ell) + dn_L(g) + dn_L(s) &= 0 \\
 dn_{L+1}(\ell) + dn_{L+1}(g) &= 0 \\
 \vdots & \\
 dn_{L+M}(\ell) + dn_{L+M}(g) &= 0 \\
 dn_{L+M+1} &= 0 \\
 \vdots & \\
 dn_N &= 0
 \end{aligned} \tag{2}$$

by Eq. (2), we find the variation relation among every phase for each component is

$$\begin{aligned}
 dn_j(s) &= -dn_j(\ell) - dn_j(g) & j &= 1, \dots, L \\
 dn_k(g) &= -dn_k(\ell) & k &= L+1, \dots, L+M \\
 dn_\ell &= 0 & \ell &= L+M+1, \dots, N
 \end{aligned}$$

substitute into equation (1) we get

$$\begin{aligned}
 & \{ \mu_1(\ell) - \mu_1(s) \} dn_1(\ell) + \{ \mu_1(g) - \mu_1(s) \} dn_1(g) \\
 & + \{ \mu_L(\ell) - \mu_L(s) \} dn_L(\ell) + \{ \mu_L(g) - \mu_L(s) \} dn_L(g) \\
 & + \{ \mu_{L+1}(\ell) - \mu_{L+1}(s) \} dn_{L+1}(\ell) \\
 & + \{ \mu_{L+M}(\ell) - \mu_{L+M}(g) \} dn_{L+M}(\ell) = 0
 \end{aligned} \tag{3}$$

In order to satisfy Eq. (3) any arbitrary values of $dn_i(\ell)$, $dn_i(g)$, and $dn_k(\ell)$, it is necessary to require the coefficient of each term be zero, that is

$$\begin{aligned}
 \mu_j(\ell) - \mu_j(s) = \mu_j(g) - \mu_j(s) &= 0 & j &= 1, \dots, L \\
 \mu_k(\ell) - \mu_k(g) &= 0 & k &= L+1, \dots, L+M
 \end{aligned}$$

Therefore, we have

$$\begin{aligned}
 \mu_j(\ell) = \mu_j(g) = \mu_j(s) & \text{ for three phases} \\
 \mu_k(\ell) = \mu_k(g) & \text{ for two phases}
 \end{aligned}$$

1.5

$$\Delta G^\circ = \sum_{i=1}^N \nu_i'' \Delta g_{f,i}^\circ - \sum_{i=1}^N \nu_i' \Delta g_{f,i}^\circ$$

ΔG° of $\frac{3}{2} O_{2(g)} \rightleftharpoons O_3$ can be computed by setting

$i=1$ for O_2 , then $\nu_1' = \frac{3}{2}$, $\nu_1'' = 0$

$i=2$ for O_3 , then $\nu_2' = 0$, $\nu_2'' = 1$

$$\therefore \Delta G^\circ = 39.06 - \frac{3}{2} \times 0 = 39.06 \text{ Kcal}$$

or $\Delta g^\circ = 39.06 \text{ Kcal/mole}$

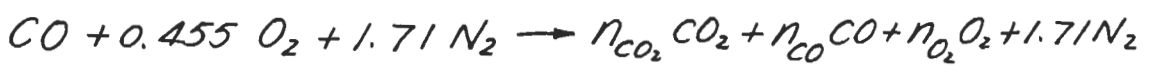
$$K_p = \exp\left(-\frac{\Delta g^\circ}{R_u T}\right) = \exp\left(-\frac{39.06 \text{ kcal/mole}}{1.9872 \frac{\text{cal}}{\text{mole K}} \times 298 \text{ K}}\right)$$

$$= e^{(-65.959)} = \frac{1}{4.422 \times 10^{28}} = 2.261 \times 10^{-29}$$

It means that at 298 K, the chance of O_2 converting into O_3 is very small. Also, since $K_p = p_{O_3} / p_{O_2}^{3/2}$, very small K_p means that the concentration of O_3 at 298 K is negligible in comparison with that of O_2 .

1.6

The reaction is



Given that products have 0.228 moles of CO

$$n_{CO} = 0.228$$

Conservation of atomic species yields

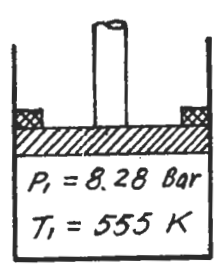
carbon : $1 = n_{CO_2} + n_{CO}$ (1)

$$\therefore n_{CO_2} = 1 - 0.228 = 0.772$$

oxygen : $1 + 2 \times 0.455 = 2 n_{CO_2} + n_{CO} + 2 n_{O_2}$ (2)

$$\therefore 1.91 = 2 \times 0.772 + 0.228 + 2 n_{O_2}$$

$$\therefore n_{O_2} = 0.069$$



Compressed gas before combustion