

## Intermediate Thermodynamics

### Exergy or Availability

#### Definitions

The first law treats all energy forms in the same way. There are, however, certain types of energy that are more valuable than others. As an example, it takes  $4 \cdot 10^{13} J$  (equivalent to  $12 GW.hr$ ) to raise the temperature of a piece of the ocean  $1 km^2$  by  $10 m$  in depth in  $1^\circ C$ . That kind of temperature gradients are frequently found in the ocean, so they present an opportunity for energy generation. However, the expected thermal efficiency of such a process to produce useful work (for example to move the shaft of a electric generator) is in the order of  $0.3 \%$ . That type of energy is simply useless to produce work. On the other hand, the same amount of energy can be obtained operating for 5 days a hydroelectric plant with  $100 m$  waterfall and a flow rate of  $100 m^3/hr$ . In this last example the efficiency to produce shaft work is close to  $90 \%$ , though the amount of energy is the same. Thus, we define the **quality** of the energy as the potential to produce useful work.

The **potential** of the energy is the maximum useful work that can be obtained from that energy in a given environment. As a consequence of the second law, the potential to produce useful energy constantly degrades.

The **dead state** of a system is the state in which it is in equilibrium with the environment. That means same temperature and pressure, no relative motion and same altitude.

The work potential of a system, relative to the dead state, is called **exergy** or **availability**.

#### Useful and Reversible Work

Consider a system in which there are a number of openings with a fluid flowing in or out, and connected to a number of  $N$  heat reservoirs and to the atmosphere at  $P_0$  and  $T_0$ . Accordingly to Eq. (1:18) for the energy conservation on a CV, we have:

$$\frac{d E_{CV}}{dt} = \dot{Q}_0 + \sum_{j=1}^N \dot{Q}_j + \dot{W}_u - P_0 \frac{dV}{dt} \Big|_{CV} + \sum_{in} \dot{m} \left( h + \frac{V^2}{2} + g z \right) - \sum_{out} \dot{m} \left( h + \frac{V^2}{2} + g z \right) \quad (1)$$

where  $\dot{W}_u$  is the useful work. A convenient expression of the entropy balance for our analysis is given by Eq. (2:27):

$$\dot{\sigma}_{tot} = \dot{\sigma}_{CV} + \dot{\sigma}_Q = \frac{dS_{CV}}{dt} - \sum_{in} \dot{m} s + \sum_{out} \dot{m} s - \frac{\dot{Q}_0}{T_0} - \sum_j \frac{\dot{Q}_j}{T_j} \quad (2)$$

Eliminating  $\dot{Q}_0$  in Eqs. (1) and (2) we get:

$$\begin{aligned} W_{act,u} = & \frac{d(E + P_0 V - T_0 S)_{CV}}{dt} - \sum_{j=1}^N \dot{Q}_j \left( 1 - \frac{T_0}{T_j} \right) + \\ & \sum_{out} \dot{m} \left( h + \frac{V^2}{2} + g z - T_0 s \right) - \sum_{in} \dot{m} \left( h + \frac{V^2}{2} + g z - T_0 s \right) + T_0 \dot{\sigma}_{tot} \end{aligned} \quad (3)$$

which gives an expression of the actual useful work in a CV in contact with  $N$  heat reservoirs at temperature  $T_j$  and the environment. An equivalent expression is obtained for a CV as a function of the temperatures at the interfaces with the heat reservoirs:

$$\begin{aligned} W_{act,u} = & \frac{d(E + P_0 V - T_0 S)_{CV}}{dt} - \sum_{i=1}^N \dot{Q}_i \left( 1 - \frac{T_0}{T_i} \right) + \\ & \sum_{out} \dot{m} \left( h + \frac{V^2}{2} + g z - T_0 s \right) - \sum_{in} \dot{m} \left( h + \frac{V^2}{2} + g z - T_0 s \right) + T_0 \dot{\sigma}_{CV} \end{aligned} \quad (4)$$

In Eqs. (3) and (4), the maximum possible work is obtained for a reversible process, in which  $\dot{\sigma}$  is 0. This, the **irreversibility** is defined as:

$$I_{tot} = W_{act} - W_{rev} = T_0 \dot{\sigma}_{tot} = T_0 (\dot{\sigma}_{CV} + \dot{\sigma}_Q) \quad (5)$$

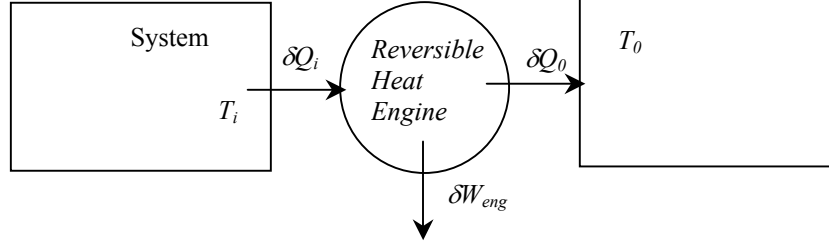
where  $\dot{\sigma}_Q$  applies if the heat reservoirs are included in the system.

The **Second-Law efficiency** or **Effectiveness** is defined taking into account the useful work that has been lost in a process. The definition is not completely unique since the useful work remaining after the process must be carefully accounted for. In general:

$$\varepsilon = 1 - \frac{\text{availability destruction and losses}}{\text{availability input}} \quad (6)$$

## Availability Transfer Associated with Heat Transfer

We analyze next the transfer (and loss) of available work in a heat transfer process. Let us consider a steady-state system with boundary temperature  $T_i$  in contact with a heat engine that rejects heat to a reservoir at  $T_0$ , as shown in Fig. 1.



**Figure 1:** two heat reservoirs exchanging heat.

The exergy of the system is the reversible work obtainable as the system evolves to the dead state. The first law states for the reversible engine:

$$\delta W_{rev} = -\delta Q_i - \delta Q_0 \quad (7)$$

and the second law requires that:

$$\frac{\delta Q_i}{T_i} = \frac{-\delta Q_0}{T_0} \quad (8)$$

Combining Eqs. (7) and (8) yields and writing for a finite heat transfer we get:

$$\delta W_{rev} = Q_i \left( 1 - \frac{T_0}{T_i} \right) \equiv \Phi_{Q,i} \quad (9)$$

where  $\Phi_{Q,i}$  is the availability or exergy transfer associated with the heat transfer  $Q_i$ . Notice that  $(1 - T_0/T_i)$  is the efficiency of a power cycle at  $T_i$  rejecting at  $T_0$ . On a rate basis, and for a number of reservoirs we write:

$$\sum_j \Phi_{Q,j} = \sum_j Q_j \left( 1 - \frac{T_0}{T_j} \right) \quad (10)$$

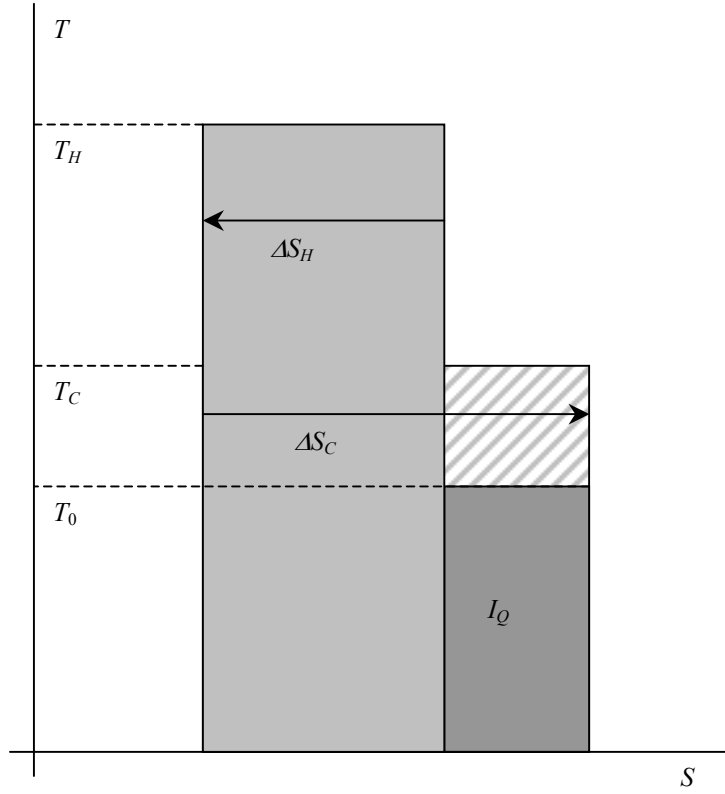
We can calculate the irreversibility from Eq. (4) assuming no work interactions and steady state:

$$I_Q = \Phi_Q = \sum_i \Phi_{Q,i} \quad (11)$$

If we are transferring heat from a reservoir at  $T_H$  to a reservoir at  $T_C$  we get:

$$I_Q = Q \left( 1 - \frac{T_0}{T_H} - 1 + \frac{T_0}{T_C} \right) = T_0 Q \left( \frac{1}{T_H} - \frac{1}{T_C} \right) \quad (12)$$

with the T-S diagram shown in Fig. 2.



**Figure 2:** graphical representation of the irreversibility in a heat transfer process from a hot to a cold reservoir.

In a general case where there is a change on the boundary temperature, we calculate the availability as the integral of Eq. (9):

$$\Phi_Q = W_{rev} = \int_1^2 \left( 1 - \frac{T_0}{T} \right) \delta Q = (U_2 - U_1) + \int_1^2 P dV - T_0 (S_2 - S_1) \quad (13)$$

with  $\delta Q = dU + PdV$ .

Let's analyze the case of a high temperature combustion heat source used for a lower temperature process in steady state and with no work exerted. The energy conservation states:

$$\dot{Q}_S = \dot{Q}_U + \sum_i \dot{Q}_i \quad (14)$$

and the availability, Eq. (4), is rewritten as:

$$0 = \dot{Q}_S \left(1 - \frac{T_0}{T_S}\right) - \dot{Q}_U \left(1 - \frac{T_0}{T_U}\right) - \sum_i \dot{Q}_i \left(1 - \frac{T_0}{T_i}\right) + I \quad (15)$$

with the subscripts  $S$ ,  $U$  and  $i$  stand for source, useful and heat loss to a reservoir at temperature  $T_i$ . Thus, the availability can be symbolically written as:

$$\Phi_{Q,S} = \Phi_{Q,U} + \sum_i \Phi_{Q,i} + I \quad (16)$$

We define the effectiveness of this process as the useful availability divided by the input availability:

$$\varepsilon = \frac{\Phi_{Q,U}}{\Phi_{Q,S}} \quad (17)$$

### Example

A high temperature source at 1000 K is used for three processes: a) heating at  $T_U=313$  K, b) Steam generation at  $T_U=473$  K and c) Furnace operation at  $T_U=693$  K. Find the efficiency and the effectiveness of these processes if the heat transfer rate is 100 kW and the heat loss to the atmosphere is 10 kW. Take the atmospheric temperature and the dead state at 300 K.

The first law efficiency is 90 % for the three cases, since only 10 % of the energy is lost in the process. As the loss occurs to the dead state, there is no availability left associated with that loss. The availabilities remaining are:

$$\Phi_{Q,S} = \dot{Q}_S \left(1 - \frac{T_0}{T_S}\right) = 70 \text{ kW}$$

$$\Phi_{Q,U} = (\dot{Q}_S - \dot{Q}_i) \left(1 - \frac{T_0}{T_U}\right) = a) 3.74, b) 32.9, c) 51 \text{ kW}$$

this means that the heating process has an effectiveness of 5.3 %, the steam generation process an effectiveness of 47 % and the furnace operation an effectiveness of 72.8 %.

### **Closed System Availability**

Eq. (4) for a closed system reduces to:

$$W_{act,u} = \frac{d(E + P_0 V - T_0 S)}{dt} - \sum_{i=1}^N \dot{Q}_i \left( 1 - \frac{T_0}{T_i} \right) + T_0 \dot{\sigma} \quad (18)$$

where  $T_i$  is the temperature at the boundary of the system. The same equation applies for a system including  $j$  thermal reservoirs, but the entropy generation term must include the transfer of heat between the process and the reservoirs (see Eq. 4). For the case of an internally reversible process we can write:

$$W_{rev,u} = \Delta E + P_0 \Delta V - T_0 \Delta S - \Phi_Q \quad (19)$$

We define the closed system availability as:

$$\Phi \equiv U - U_0 + P_0 (V - V_0) - T_0 (S - S_0) + \frac{m}{2} V^2 + m g z \quad (20)$$

so the actual useful work can be calculated as:

$$W_{act,u} = \Phi_2 - \Phi_1 - \Phi_Q + I_{CM} \quad (21)$$

The total irreversibility is:

$$I_{tot} = W_{act,u} - W_{rev,u} \quad (22)$$

replacing the corresponding terms we get:

$$I_{tot} = W_{act,tot} + P_0 \Delta V - (\Delta U + P_0 \Delta V - T_0 \Delta S) + \sum_j \dot{Q}_j \left( 1 - \frac{T_0}{T_j} \right) \quad (23)$$

using the first law ( $W_{act,tot} - \Delta U = -Q = -Q_0 - \sum_j \dot{Q}_j$ ) and dropping the terms that cancel out we get:

$$I_{tot} = -Q_0 + T_0 \Delta S - \sum_j \dot{Q}_j \frac{T_0}{T_j} \quad (24)$$

where the heat interactions are  $Q_j = T_j \Delta S_j$ . Replacing we get the final expression:

$$I_{tot} = T_0 \left( \Delta S_0 + \Delta S_{CM} - \sum_j \Delta S_{R,j} \right) = T_0 \Delta S_{tot} \quad (25)$$

### Some Examples

Oxygen initially at 300 K and 100 kPa is contained in a rigid tank. Two processes are considered to increase its temperature to 500 K: a) the gas receives energy by a paddle wheel adiabatically and b) by means of an external heat reservoir at 600 K, with a system boundary temperature taken as the gas temperature. Determine 1) the availability change, 2) the irreversibility (kJ/kmol) and 3) the effectiveness of the process. Take  $T_0=300$  K.

- (a) (1) The availability change is obtained using Eq. (20) in specific form for the initial and final states.

$$\Delta\phi = u_2 - u_1 + P_0(v_2 - v_1) - T_0(s_2 - s_1) + \frac{m}{2}(V_2^2 - V_1^2) + m g(z_2 - z_1) =$$

$$4372 + 0 - 300 \cdot 11.13 = 1033 \text{ kJ / kmol}$$

A reversible process ( $\Delta s=0$ ) would give  $\Delta\phi = \Delta u = 4372 \text{ kJ / kmol}$ , since all the internal energy is provided by the paddle wheel.

- (2) from Eq. (21) in specific form, the irreversibility change is:

$$I_{CM} = w_{act,u} - \phi_2 + \phi_1 + \phi_Q = 4372 - 1033 + 0 = 3339 \text{ kJ / kmol}$$

that equals  $T_0 \Delta s$ , in accordance to Eq. (25).

- (3) the effectiveness is:

$$\varepsilon_a = \frac{\text{outcome}}{\text{input}} = \frac{\Delta\phi}{w} = \frac{1033}{4372} = 0.236$$

- (b) (1) Being a function of the state, the change in availability is the same as in the previous case. The change (loss) in availability of the heat reservoir is:

$$\phi_R = q_R \left( 1 - \frac{T_0}{T_R} \right) = -4372 \left( 1 - \frac{300}{600} \right) = -2186 \text{ kJ / kmol}$$

- (2) The total irreversibility is expressed as:

$$I_{CM} = w_{act,u} - \sum (\phi_2 - \phi_1) + \phi_Q = 0 - (1033 - 2186) + 0 = 1153 \text{ kJ / kmol}$$

(3) The effectiveness, as defined before, is:

$$\varepsilon_b = \frac{\Delta\phi}{\phi_R} = \frac{1033}{2186} = 0.473$$

CO<sub>2</sub> is adiabatically compressed from 10 bar, 300 K to 50 bar, 450 K. Determine 1) the availability change, 2) the irreversibility and 3) the effectiveness for (a) ideal gas and (b) real gas.

(a) For the ideal gas we have:

$$\Delta\phi = u_2 - u_1 + P_0(v_2 - v_1) - T_0(s_2 - s_1) =$$

$$u_2 - u_1 + R P_0 \left( \frac{T_2}{P_2} - \frac{T_1}{P_1} \right) - T_0 \left( s_2^0 - s_1^0 - R \ln \frac{P_2}{P_1} \right)$$

(1) substitution of the ideal gas data for CO<sub>2</sub> (R=8.3145 kJ/kmol K, molar mass 44.02 kg/kmol) gives:

$$\Delta\phi = 4803 - 175 - 864 = 3764 \text{ kJ/kmol} = 85.53 \text{ kJ/kg}$$

(2) The irreversibility can be calculated using Eq. (22), where the actual useful work is given by  $u_2 - u_1 + P_0(v_2 - v_1)$ . Therefore:

$$I_{CM} = w_{act,u} - w_{rev,u} = (4803 - 175) / 44.02 - 85.53 = 19.63 \text{ kJ/kg}$$

(3) The effectiveness is calculated as exergy change/input work, thus:

$$\varepsilon = \frac{\Delta\phi}{\Delta u} = \frac{85.53}{109.13} = 0.784$$

(b) Using real gas data, we obtain (1)  $\Delta\phi = 80.9 \text{ kJ/kg}$ , (2)  $I_{CM} = 15.06 \text{ kJ/kg}$  and

$$(3) \varepsilon = 80.92 / 99.76 = 0.81$$

### **Availability in a Steady-State Control Volume**

In a steady-state process, Eq. (3) for a CV in contact with  $j$  heat reservoirs gives:

$$W_{act,u} = \sum_{out} m \left( h + \frac{V^2}{2} + g z - T_0 s \right) - \sum_{in} m \left( h + \frac{V^2}{2} + g z - T_0 s \right) -$$

$$\sum_{j=1}^N \dot{Q}_j \left( 1 - \frac{T_0}{T_j} \right) + T_0 \sigma_{tot} \quad (26)$$

Eq. (26) can be written in compact form as:



$$W_{act,u} = \sum_{out} \dot{m} b - \sum_{in} \dot{m} b - \sum_{j=1}^N \dot{Q}_j \left( 1 - \frac{T_0}{T_j} \right) + \dot{I}_{tot} \quad (27)$$

where  $b = h + ke + pe + T_0 s$ . For the very important case of a reversible process with only one input and one output, in specific form we write:

$$w_{rev} = \left( h + \frac{V^2}{2} + g z - T_0 s \right)_2 - \left( h + \frac{V^2}{2} + g z - T_0 s \right)_1 - \sum_{j=1}^N q_j \left( 1 - \frac{T_0}{T_j} \right) \quad (28)$$

It is then natural to define the **stream** or **flow availability** as the maximum work that can be obtained as the fluid is changed reversible to the dead state while exchanging heat solely with the environment. Thus the stream availability is:

$$\psi = (h - h_0) + \frac{(V - V_0)^2}{2} + g(z - z_0) - T_0(s - s_0) \quad (29)$$

Notice that Eq. (29) express the thermomechanical effects only, excluding chemical mass, energy and entropy transfers. For an ideal gas, Eq. (29) can be written as:

$$\frac{\psi}{c_p T_0} = \frac{T}{T_0} + \ln \frac{T}{T_0} + \ln \left( \frac{P}{P_0} \right)^{(k-1)/k} \quad (30)$$

We can now rewrite Eq. (4) as a general availability balance in a CV:

$$\frac{d\Phi_{CV}}{dt} = \sum_i \dot{Q}_i \left( 1 - \frac{T_0}{T_i} \right) + \sum_{in} \dot{m} b - \sum_{out} \dot{m} b + \left( W_{act} + P_0 \frac{dV_{CV}}{dt} \right) - \dot{I}_{CV} \quad (31)$$

or in symbols, for a steady-state process with only one input and one exit we get:

$$0 = \Phi_Q - \dot{m} \Delta\psi + \dot{W}_{act} - \dot{I}_{CV} \quad (32)$$

In Eq. (31) we have that the closed system exergy change within the CV is due to exergy transfer due to heat transfer, convective influx or outflow of exergy, external work and work against the atmosphere at  $P_0$ , minus the losses due to irreversibilities within the CV.

The irreversibility follows from Eq. (3.51). In steady flow:

$$I_{CV} = T_0 \sigma_{CV} = \sum_i \dot{Q}_i \left( 1 - \frac{T_0}{T_i} \right) + \sum_{in} \dot{m} b - \sum_{out} \dot{m} b + \dot{W}_{act} \quad (33)$$

Finally, the case of a steady-state, one inlet (1)-one exit (2) system satisfies:

$$\dot{W}_{act} = \dot{\Psi}_2 - \dot{\Psi}_1 - \sum_i^N \dot{Q}_i \left( 1 - \frac{T_0}{T_i} \right) + T_0 \sigma_{CV} \quad (34)$$

## **Turbines**

For a steady state gas turbine, the first law states:

$$q + w = h_o - h_i + ke_e - ke_i \quad (35)$$

The case of a isentropic turbine implies adiabatic expansion, which means that the work is expressed as ( $q=0$ , negligible kinetic energy):

$$w = h_{os} - h_i \quad (36)$$

where  $h_{os}$  stands for the enthalpy at the exit assuming isentropic flow. A T-s graph is shown in Fig. 3. The shaded area below line  $P_i$  between states  $i$  and  $A$  equals  $h_{os} - h_i$ . Since the process is at constant pressure,  $T ds = dh - v dP = dh$  (second  $Tds$  equation). In an actual process, the end point  $2a$  will be attained with the corresponding change in entropy. Using similar derivations, the area shaded in mid-dark gray represents the work done by frictional forces and that results in a loss of availability. However, this frictional work is mostly converted to heat (frictional heating) and some converted to turbulence. If the temperature remains above  $T_0$ , then part of the frictional heating can be converted back to work using a Carnot engine, thus resulting in an increment of exergy. This additional theoretical work is shown by the area between  $os$  and  $oa$  and above  $T_0$ . The corresponding part below  $T_0$  is the irreversibility,  $T_0(s_{oa}-s_i)$ .

The turbine effectiveness is calculated as:

$$\varepsilon = \frac{\text{outcome}}{\text{input}} = \frac{\dot{W}_{shaft}}{\dot{\Psi}_o - \dot{\Psi}_i} \quad (37)$$



$$i_{CV} = -(\psi_2 - \psi_1) + q \left( 1 - \frac{T_0}{T_b} \right) + w_{act} =$$

$$-(-854.7) + (-29.8) \left( 1 - \frac{298}{573} \right) + (-746) = 94.4 \text{ kJ / kg}$$

(3) The effectiveness is defined as the actual output divided the maximum possible work output, or outcome/input. Thus:

$$\varepsilon = \frac{w_{act}}{\Delta\psi} = 0.873$$

(b) The change in stream availability is the same as the case before. The irreversibility can be calculated using  $T_0$  instead of  $T_b$  which gives 108.7 kJ/kg. The difference with the previous case is the irreversibility due to heat transfer, or the exergy associated to heat transfer.

## **Compressors and Pumps**

The same type of analysis done for the turbines can be applied for a compressor or pump. The effectiveness is now defined as:

$$\varepsilon = \frac{\Delta\psi}{w_{act}} \quad (38)$$

### ***Example***

Water at 0.1 MPa undergoes a pressure rise of 1.0 MPa in a pump with a first law efficiency of 70 %. Determine the irreversibility of the process and the second-law efficiency. Use an inlet temperature of 50 °C and  $T_0=20^\circ\text{C}$ .

The properties can be calculated from a steam table for the inlet condition and the isentropic exit condition. For the inlet condition:

$$h_1 = 209.4 \text{ kJ / kg}, s_1 = 0.7038 \text{ kJ / kg} \cdot \text{K}, \psi_1 = 6.0 \text{ kJ / kg}, v_1 = 1.0121 \text{ cm}^3 / \text{g}$$

at the exit:

$$T_{2s} = 50.04 \text{ C}, h_{2s} = 210.4 \text{ kJ / kg}, s_2 = 0.7038 \text{ kJ / kg} \cdot \text{K}, v_2 = 1.0117 \text{ cm}^3 / \text{g}$$

The actual exit enthalpy can be calculated from the definition of first law efficiency:

$$h_{2a} = h_1 + \frac{h_{2s} - h_1}{\eta} = 210.88 \text{ kJ / kg}$$

And using this enthalpy and the exit pressure we get:

$$T_{2a} = 50.15 \text{ C}, \psi_{2a} = 7.062 \text{ kJ / kg}, s_{2a} = 0.7052 \text{ kJ / kg} \cdot \text{K}, v_2 = 1.0117 \text{ cm}^3 / \text{g}$$

The irreversibility is then:

$$i = T_0 \Delta s = 0.410 \text{ kJ / kg}$$

The second-law efficiency is then:

$$\varepsilon = \frac{\Delta\psi}{w_{act}} = \frac{7.062 - 6}{210.88 - 209.4} = 0.717$$

