CH365 Chemical Engineering Thermodynamics

Lesson 24
Open Systems and Calculation of Work

What is Entropy?

Lazare Carnot, 1753 – 1823

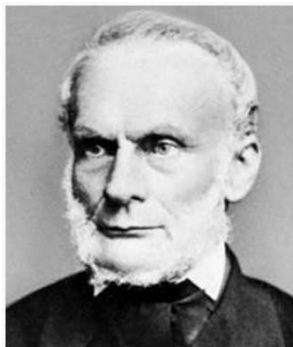https://en.wikipedia.org/wiki/Lazare_Carnot

1803 *Fundamental Principles of Equilibrium and Movement -* in any machine, the accelerations and shocks of the moving parts represent losses of *moment of activity (lost work)*.

Sadi Carnot 1796 – 1832

https://en.wikipedia.org/wiki/Nicolas_L%C3%A9onard_Sadi_Carnot

1824 *Reflections on the Motive Power of Fire* – in all heat engines, whenever "caloric" (heat) falls across a temperature difference, work is produced

Rudolf Clausius 1822 – 1888

https://https://en.wikipedia.org/wiki/Rudolf_Clausius

1850s and 1860s – gave a mathematical interpretation by questioning the nature of the inherent loss of usable heat when work is done, e.g. heat produced by friction

Exergy and Anergy

Terms not used in this class but still common and important

Strictly second-law properties

In thermodynamics, the **exergy** of a system is the maximum useful work possible during a process that brings the system into equilibrium with a heat reservoir. When the surroundings are the reservoir, **exergy** is the potential of a system to cause a change as it achieves equilibrium with its environment.

Exergy – Wikipedia

https://en.Wikipedia.org/wiki/Exergy

Suppose a Carnot heat engine has a heat source temperature of 500K and ambient heat sink temperature of 300K. Then the Carnot efficiency will be 1–300/500=40%. If 10 Joules of heat energy is transferred at 500K then exergy is 4J and "anergy" is 6J.

Difference between Gibbs free energy and exergy?

https://www.quora.com/What-is-the-difference-between-exergy-and-energy

$$\Delta G = \Delta H - T \cdot \Delta S \qquad \Delta B = \Delta H - T_0 \cdot \Delta S \qquad W_{ideal} = \Delta H - T_\sigma \Delta S$$

(Eq. 5.22)

It is <u>very important</u> for us to see where these concepts come from.

Mathematical Statement - 2nd Law

Every process proceeds in such a direction that the _total_ entropy change associated with it is positive. A limiting value of zero is obtained for a reversible process. No process is possible for which the entropy change decreases.

$$\Delta S_{total} \geq 0$$

(Eq. 5.2)

With respect to the H and C reservoirs,

In a heat engine cycle:

$$\Delta U = Q + W = Q_H + Q_C + W = 0$$

$$\Delta S_{total} = \frac{-Q_H}{T_H} - \frac{Q_C}{T_C}$$

$$W = -Q_H - Q_C$$

General equation for work of a heat engine:

$$W = Q_C\left(\frac{T_H - T_C}{T_C}\right) + T_H \Delta S_{total}$$

$$T_H \Delta S_{total} = -Q_H - Q_C\frac{T_H}{T_C}$$

$$-Q_H = Q_C\frac{T_H}{T_C} + T_H \Delta S_{total}$$

$$W = Q_C\frac{T_H}{T_C} + T_H \Delta S_{total} - Q_C$$

$$W = Q_C\left(\frac{T_H}{T_C} - 1\right) + T_H \Delta S_{total}$$

$$W = Q_C\left(\frac{T_H - T_C}{T_C}\right) + T_H \Delta S_{total}$$

(p. 181, lesson 22)

Mathematical Statement - 2nd Law

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$$\Delta S_{total} \geq 0$$

(Eq. 5.2)

Slightly different derivation:

Cyclic heat engine:

$$\Delta U = Q + W = Q_H + Q_C + W = 0$$

$$\Delta S_{total} = \frac{-Q_H}{T_H} - \frac{Q_C}{T_C}$$

$$W = -Q_H - Q_C$$

General equation for work of a heat engine:

$$W = -Q_H \left(\frac{T_C - T_H}{T_C} \right) + T_C \Delta S_{total}$$

$$T_C \Delta S_{total} = -Q_H \frac{T_C}{T_H} - Q_C$$

$$-Q_C = Q_H \frac{T_C}{T_H} + T_C \Delta S_{total}$$

$$W = -Q_H + Q_H \frac{T_C}{T_H} + T_C \Delta S_{total}$$

$$W = Q_H \left(\frac{T_C}{T_H} - 1 \right) + T_C \Delta S_{total}$$

$$W = -Q_H \left(\frac{T_H - T_C}{T_H} \right) + T_C \Delta S_{total}$$

(p. 181, lesson 22)

Example 5.1

A 40-kg steel casting (C_P = 0.5 kJ kg^{-1} K^{-1}) at a temperature of 450 deg C is quenched in 150 kg of oil (C_P = 2.5 kJ kg^{-1} K^{-1}) at 25 deg C. If there are no heat losses, what is the change in entropy of (a) the casting, (b) the oil, and (c) both considered together?

Start with a (level 1) enthalpy balance to determine the final temperature:

$$\Delta H_{cast} + \Delta H_{oil} = 0$$

$$m_{cast}C_{P,cast}\left(T_{final} - T_{initial}^{cast}\right) + m_{oil}C_{P,oil}\left(T_{final} - T_{initial}^{oil}\right) = 0$$

$$40 \cdot (0.5) \cdot \left(T_{final} - 723.15\right) + 150 \cdot (2.5) \cdot \left(T_{final} - 298.15\right) = 0$$

$$T = 319.67 \text{ K} = 46.52 \text{ degC}$$

Example 5.1, Continued

(a) Change in entropy of the casting: pressure term has been dropped from Eq. 5.10

$$\Delta S_{cast} = m_{cast} \int_{T_{0,cast}}^{T_{final}} \frac{C_{P,cast}}{T} dT = m_{cast} C_{P,cast} \ln\left(\frac{T_{final}}{T_{0,cast}}\right) = 40 \cdot 0.5 \cdot \ln\left(\frac{319.67}{723.15}\right) = -16.33 \frac{kJ}{K}$$

(b) Change in entropy of the oil:

$$\Delta S_{oil} = m_{oil} \int_{T_{0,oil}}^{T_{final}} \frac{C_{P,oil}}{T} dT = m_{oil} C_{P,oil} \ln\left(\frac{T_{final}}{T_{0,oil}}\right) = 150 \cdot 2.5 \cdot \ln\left(\frac{319.67}{298.15}\right) = +26.13 \frac{kJ}{K}$$

(c) Both together:

$$\Delta S_{both} = \Delta S_{cast} + \Delta S_{oil} = -16.33 + 26.13 = 9.80 \frac{kJ}{K}$$

Entropy Balance for Open System

$$\left\{\begin{array}{c}\text{Net rate of}\\\text{change in}\\\text{entropy of}\\\text{flowing streams}\end{array}\right\} + \left\{\begin{array}{c}\text{Time rate of}\\\text{change in}\\\text{entropy in}\\\text{control volume}\end{array}\right\} + \left\{\begin{array}{c}\text{Time rate of}\\\text{change in}\\\text{entropy in}\\\text{surroundings}\end{array}\right\} = \left\{\begin{array}{c}\text{Total rate of}\\\text{entropy}\\\text{generation}\end{array}\right\}$$

p. 191

(calculated with eq. 5.10)

$$\Delta\left(S\dot{m}\right)_{fs} + \frac{d(mS)_{CV}}{dt} + \frac{dS^t_{surr}}{dt} = \dot{S}_G \geq 0 \qquad \text{Eq. 5.15}$$

$$\Delta\left(S\dot{m}\right)_{fs} + \frac{d(mS)_{CV}}{dt} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geq 0 \qquad \text{Eq. 5.16}$$

steady-state

$$\Delta\left(S\dot{m}\right)_{fs} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geq 0 \qquad \text{Eq. 5.17}$$

to be used in slides 14 and 16

one exit and one entrance,
with constant flow rate,
and dividing by $\dot{m}$

$$\Delta S - \sum_j \frac{Q_j}{T_{\sigma,j}} = S_G \geq 0 \qquad \text{Eq. 5.18}$$

Uniform surrounding
temperature.

$$\Delta S - \frac{Q}{T_{\sigma}} = S_G \geq 0 \qquad \text{Eq. 5.33}$$
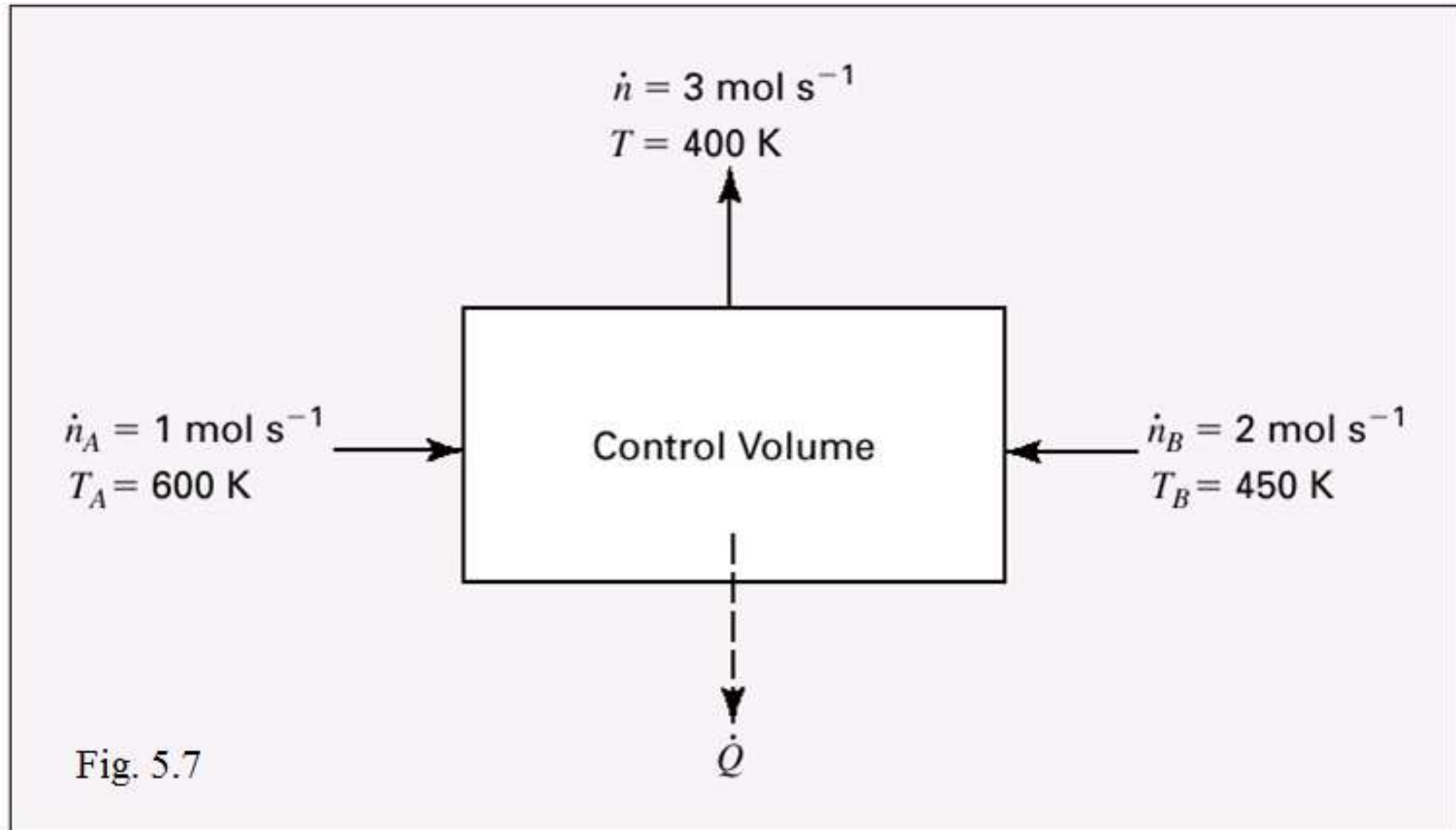
Presented out of
sequence on p. 200.

Example 5.5

In a steady-state flow process, 1 mol/s of air at 600 K and 1 atm is continuously mixed with 2 mol/s of air at 450 K and 1 atm. The product stream is at 400 K and 1 atm. A schematic representation of the process is shown in Fig. 5.7. Determine the rate of heat transfer and rate of entropy generation for the process. Assume that air is ideal with C_P=7/2R, and that the surroundings are at 300 K, and that kinetic and potential energy changes are negligible.

Example 5.5

$\dot{n} = 3$ mol s^{-1}
$T = 400$ K

$\dot{n}_A = 1$ mol s^{-1}
$T_A = 600$ K

Control Volume

$\dot{n}_B = 2$ mol s^{-1}
$T_B = 450$ K

$\dot{Q}$

Fig. 5.7

Example 5.5, Continued

Energy (Enthalpy) Balance

Eq. 2.30, no change in velocity or height, no shaft work

$$\Delta\left[(H + \tfrac{1}{2}u^2 + zg)\dot{n}\right]_{fs} = \dot{Q} + \dot{W}_s$$

$$\dot{Q} = \dot{n}H - \dot{n}_A H_A - \dot{n}_B H_B$$

$$= \dot{n}_A\left(H - H_A\right) + \dot{n}_B\left(H - H_B\right) \qquad \dot{n} = \dot{n}_A + \dot{n}_B$$

$$= \dot{n}_A C_P\left(T - T_A\right) + \dot{n}_B C_P\left(T - T_B\right) \qquad H = C_P\left(T - T_{REF}\right)$$

$$= C_P\left[\dot{n}_A\left(T - T_A\right) + \dot{n}_B\left(T - T_B\right)\right]$$

$$= (7/2)(8.314)\left[(1)(400 - 600) + 2(400 - 450)\right]$$

$$= -8{,}729.7\,\mathrm{Js}^{-1}$$

Example 5.5, Continued

Entropy Balance

$$\dot{S}_G = \dot{n}S - \dot{n}_A S_A - \dot{n}_B S_B - \frac{\dot{Q}}{T_\sigma} \qquad \text{Eq. 5.17}$$

$$= \dot{n}_A \left(S - S_A \right) + \dot{n}_B \left(S - S_B \right) - \frac{\dot{Q}}{T_\sigma} \qquad \dot{n} = \dot{n}_A + \dot{n}_B$$

$$\Delta S = S - S_A$$

$$= \int_{T_A}^{T} \frac{C_P}{T} dT$$

$$= C_P \ln\left(T \right)\big|_{T_A}^{T}$$

$$= \dot{n}_A C_P \ln\left(\frac{T}{T_A} \right) + \dot{n}_B C_P \ln\left(\frac{T}{T_B} \right) - \frac{\dot{Q}}{T_\sigma} \qquad S = C_P \ln\left(T / T_{REF} \right)$$

The entropy change of a system resulting only from transfer of heat can always be calculated by $\int dQ / T$ whether the heat transfer is accomplished reversibly or not.

$$= C_P \left[\dot{n}_A \ln\left(\frac{T}{T_A} \right) + \dot{n}_B \ln\left(\frac{T}{T_B} \right) \right] - \frac{\dot{Q}}{T_\sigma}$$

$$= \left(7/2 \right)\left(8.314 \right) \left[\left(1 \right)\ln\left(\frac{400}{600} \right) + \left(2 \right)\ln\left(\frac{400}{450} \right) \right] + \frac{8,729.7}{300}$$

$$= 10.446 \, J\,mol^{-1}\,s^{-1}$$

Calculation of Ideal Work

$$\Delta\left(S\dot{m}\right)_{fs} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geq 0 \qquad \text{reversible}$$

(Eq. 5.17 from slide 9)

to be used again in slide 16

Limiting case:
reversible and uniform
surrounding temperature.

$$\Delta\left(S\dot{m}\right)_{fs} - \frac{\dot{Q}}{T_{\sigma}} = 0 \qquad\qquad \dot{Q} = T_{\sigma}\Delta\left(S\dot{m}\right)_{fs}$$

$$\Delta\left[\left(H + \tfrac{1}{2}u^2 + zg\right)\dot{m}\right]_{fs} = \dot{Q} + \dot{W}_S \qquad \text{(Eq. 2.30)}$$

(rev)

$$\Delta\left[\left(H + \tfrac{1}{2}\cancel{u^2} + \cancel{zg}\right)\dot{m}\right]_{fs} = T_{\sigma}\Delta\left(S\dot{m}\right)_{fs} + \dot{W}_S \qquad \text{(Eq. 5.19)}$$

ignore kinetic and
potential energy terms:

to be used in slide 16

$$\dot{W}_S = \Delta\left(H\dot{m}\right)_{fs} - T_{\sigma}\Delta\left(S\dot{m}\right)_{fs} \qquad \text{(Eq. 5.20)}$$

ideal; completely
reversible   "$\dot{W}_{ideal}$"

$$\dot{W}_{ideal} = \dot{m}\left(\Delta H - T_{\sigma}\Delta S\right) \qquad \text{(Eq. 5.21)}$$

$$W_{ideal} = \frac{\dot{W}_{ideal}}{\dot{m}} = \Delta H - T_{\sigma}\Delta S \qquad \text{(Eq. 5.22)}$$

Example 5.7

What is the maximum work that can be obtained in a steady-state flow process from 1 mol of nitrogen at 800 K and 50 bar? Assume the nitrogen is an ideal gas and take the temperature and pressure of the surroundings as 300 K and 1.0133 bar.

(Eq. 4.8, p. 143)

$$\Delta H = \int_{T0}^{T} C_P^{ig} dT$$

$$\Delta H = 8.314 \cdot ICPH = -15,060 \tfrac{J}{mol}$$

(L23, Eq. 5.11)

$$\Delta S = \int_{T1}^{T2} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_2}{P_1} = R \cdot ICPS - R \ln \frac{P_2}{P_1}$$

$$\Delta S = -29.371 - 8.314 \cdot \ln \frac{1.0133}{50} = 3.044 \tfrac{J}{mol \cdot K}$$

$$W_{ideal} = \Delta H - T_\sigma \Delta S \qquad = 15,060 - (300) \cdot (3.042) = -15,973 \tfrac{J}{mol}$$

(Eq. 5.22)

Calculation of "Lost Work"

work wasted as a result of irreversibilities

$$W_{lost} \equiv W_S - W_{ideal} \quad \text{(Eq. 5.25)}$$

$$\dot{W}_{lost} \equiv \dot{W}_S - \dot{W}_{ideal} \quad \text{(Eq. 5.26)}$$

$$\dot{W}_S = \Delta\left[\left(H + \tfrac{1}{2}u^2 + zg\right)\dot{m}\right]_{fs} - \dot{Q} \quad \text{(Eq. 2.30)}$$

$$\dot{W}_{ideal} = \Delta\left[\left(H + \tfrac{1}{2}u^2 + zg\right)\dot{m}\right]_{fs} - T_\sigma \Delta\left(S\dot{m}\right)_{fs} \quad \text{(Eq. 5.19)}$$

$$\dot{W}_{lost} \equiv T_\sigma \Delta\left(S\dot{m}\right)_{fs} - \dot{Q} \quad \text{(Eq. 5.27)}$$

RHS equal

$$\dot{S}_G = \Delta\left(S\dot{m}\right)_{fs} - \frac{\dot{Q}}{T_\sigma} \quad \begin{array}{l}\text{(Eq. 5.28)}\\ \text{(Eq. 5.17 from slide 9 w/ one } T_\sigma)\end{array}$$

$$T_\sigma \cdot \dot{S}_G = T_\sigma \cdot \Delta\left(S\dot{m}\right)_{fs} - \dot{Q}$$

Therefore,

$$\dot{W}_{lost} = T_\sigma \dot{S}_G \quad \text{(Eq. 5.29)}$$

Calculation of Lost Work

Engineering significance: The greater the irreversibility of a process, the greater the rate of entropy production, and the greater the amount of energy that becomes unavailable for work.

$\dot{W}_{lost} = \dot{m}\,T_\sigma\,\Delta S - \dot{Q}$ (Eq. 5.30)	$W_{lost} = T_\sigma\,\Delta S - Q$ (Eq. 5.31)
$\dot{S}_G = \dot{m}\,\Delta S - \dfrac{\dot{Q}}{T_\sigma}$ (Eq. 5.32)	$S_G = \Delta S - \dfrac{Q}{T_\sigma}$ (Eq. 5.33)

This also means lost work is zero for a reversible process.

$$W_{lost} = T_\sigma S_G \quad \text{(Eq. 5.29, previous slide, } \div \dot{m}\text{)}$$

$$S_G = \Delta S - \frac{Q}{T_\sigma} \quad \text{(Slide 9)}$$

$$W_{lost} = T_\sigma S_G = T_\sigma\left(\Delta S - \frac{Q}{T_\sigma}\right) = T_\sigma \Delta S - Q$$

Questions?