

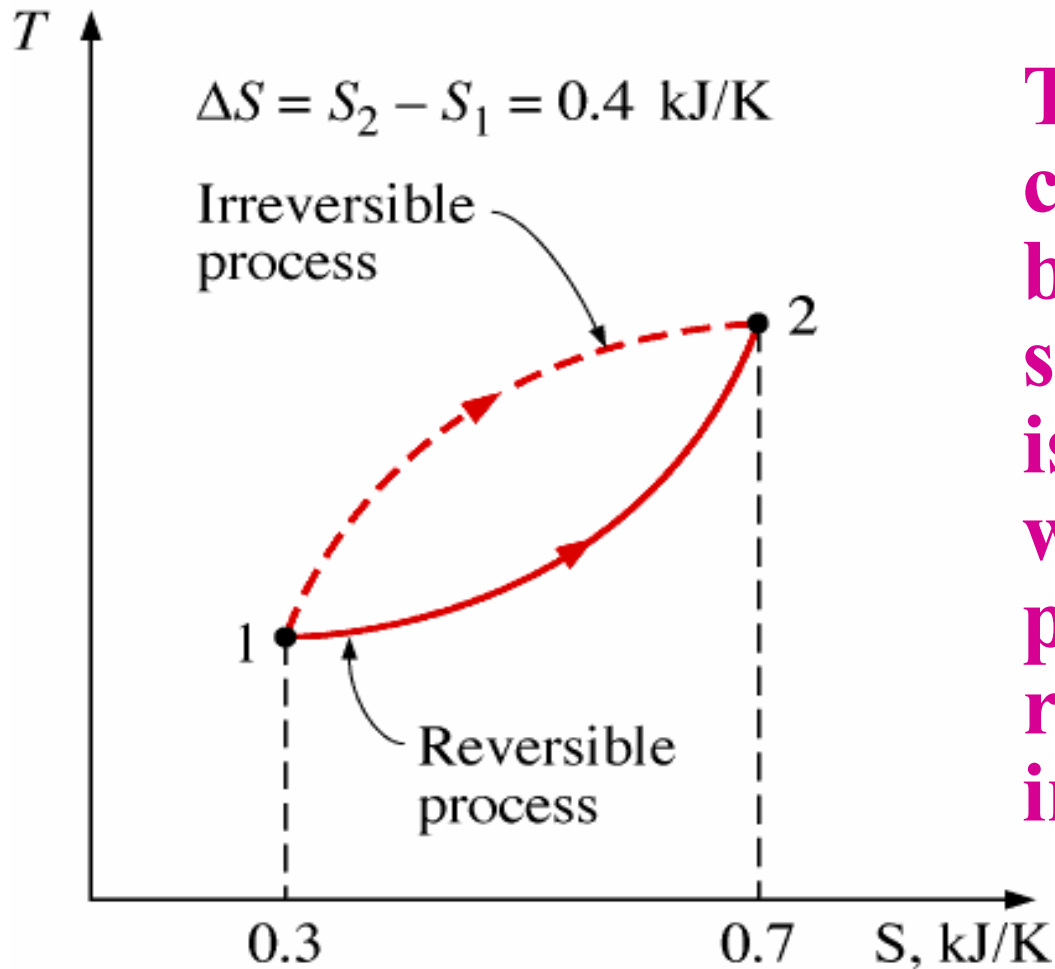
The T-dS

Equations & Diagrams

Meeting 9

Section 4-3 & 4-4

*The Entropy is a **PROPERTY***



The entropy change between two specific states is the same whether the process is reversible or irreversible

We can write entropy change as an equality by adding a new term:

$$\Delta S_{1,2} = \int_1^2 \left(\frac{\delta Q}{T} \right)_A + S_{\text{gen}} \left(\frac{\text{Joules}}{\text{K}} \right)$$

entropy change, $\Delta S \geq 0$ or < 0

entropy transfer due to heat transfer, $Q \geq 0$ or < 0

entropy generation or production, $S_{\text{gen}} \geq 0$

$S_{\text{gen}} \geq 0$; not a property. The larger the irreversibilities, the greater the value of the entropy production

- $S_{\text{gen}} > 0$ is an actual irreversible process.
- $S_{\text{gen}} = 0$ is a reversible process.
- $S_{\text{gen}} < 0$ is an impossible process.

The Tds Equations



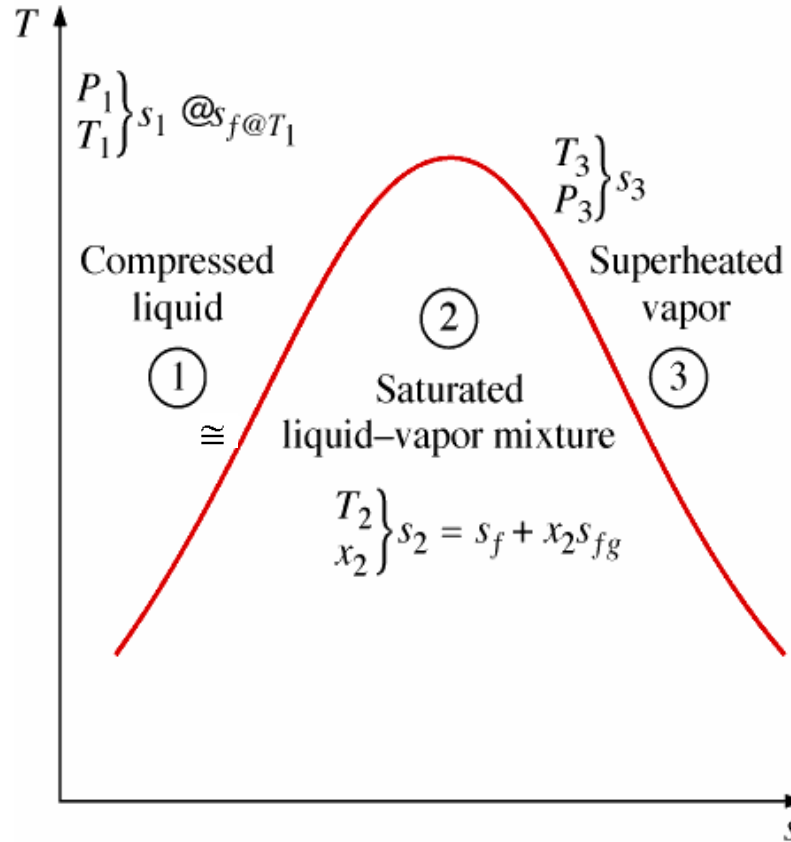
In previous slides, we developed a new property, entropy

$$s_2 - s_1 = \int_1^2 \left(\frac{\delta q}{T} \right)_{int \ rev}$$

Units are $\frac{kJ}{kg \cdot K}$ ***or*** $\frac{Btu}{lbm \cdot R}$

The Entropy Change of a Pure Substance

The entropy of a pure substance is determined from the tables, just as for any other property

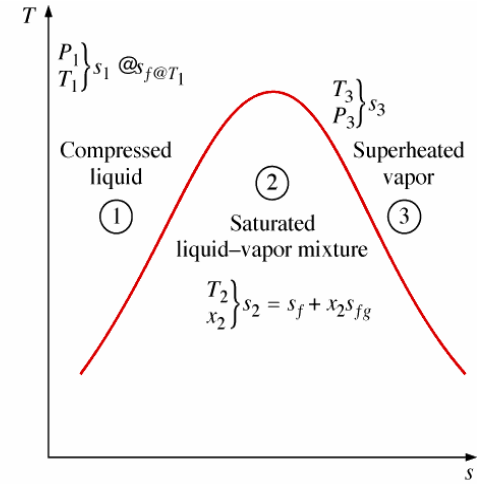
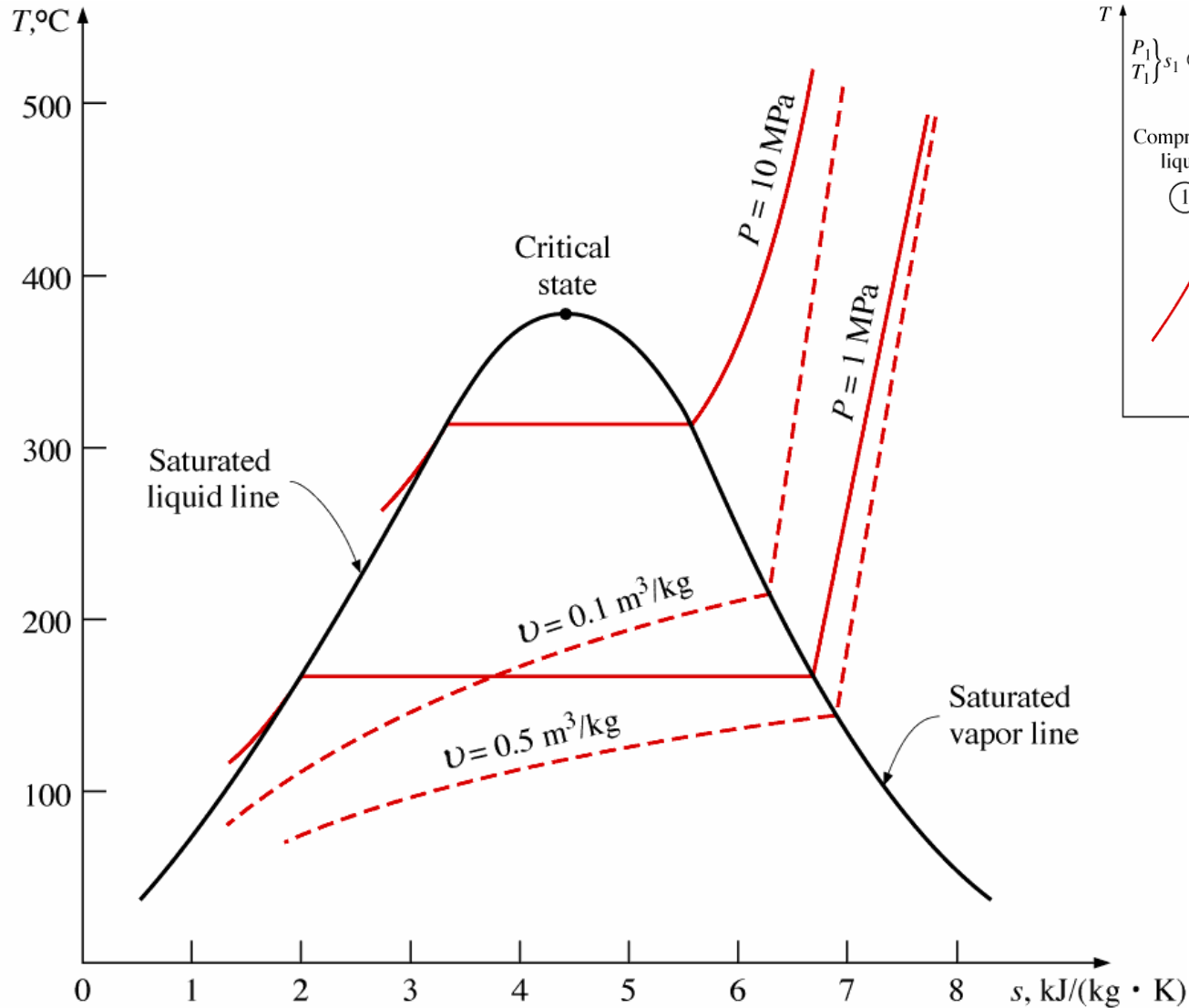


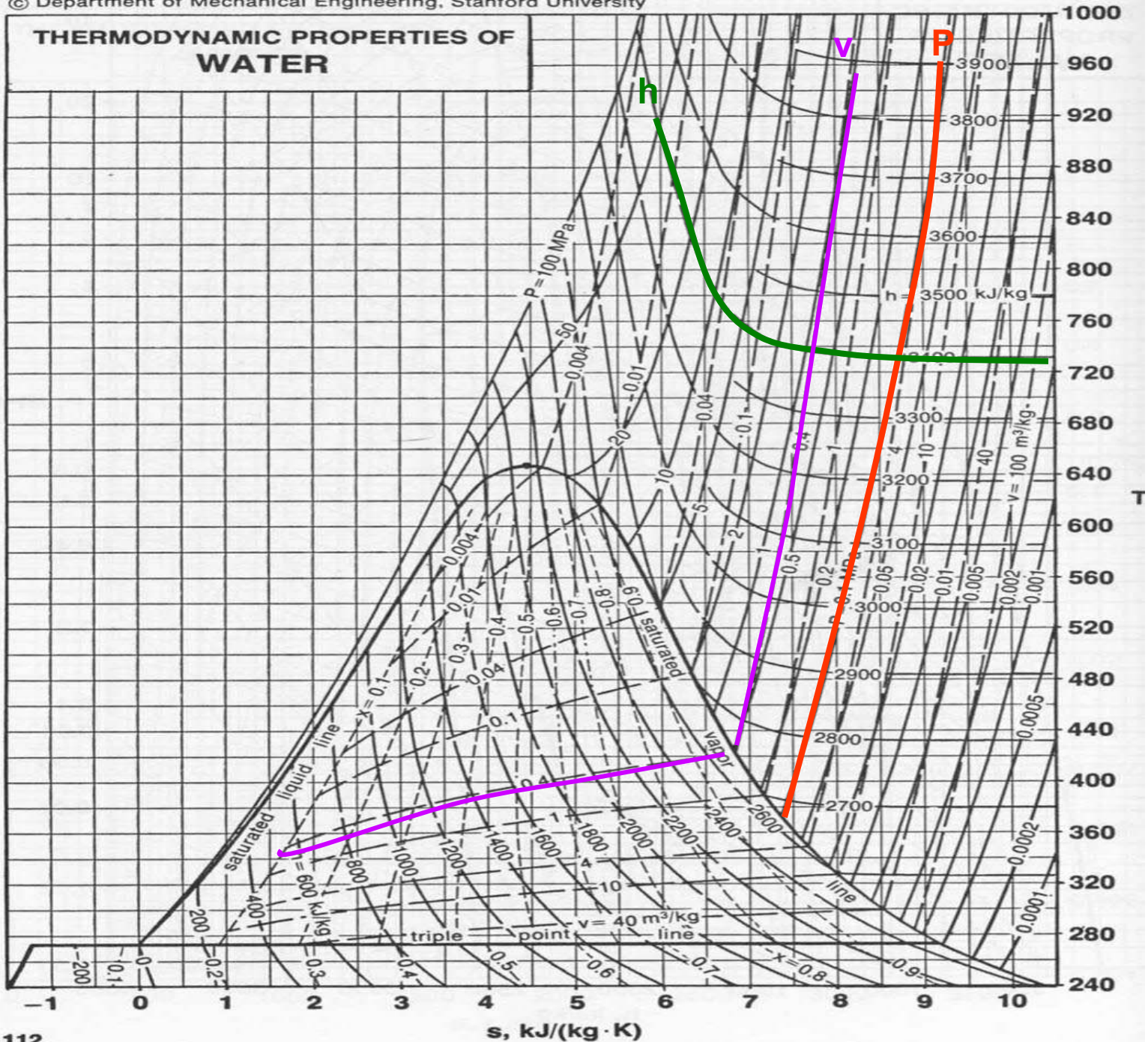
It is tabulated just like u, v, and h: $s = s_f + x(s_g - s_f)$

And, for compressed or subcooled liquids,

$$s(T, p) \cong s_f(T)$$

T-s Diagram for Water





TEAMPLAY

- Use the thermodynamic tables from your book to find the entropy of the water at:
- 50 kPa and 500°C. Specify the units.
- 9,1546 kJ/Kkg (super-aquecido)
- 100°C and a quality of 50%. Specify the units.
- (1,3069+7,3549)/2 kJ/Kkg (saturado)
- 1 MPa and 120°C. Specify the units .
- 1,5276 kJ/Kkg (liq. Comprimido)

T-s diagram

Recall that the P-v diagram was very important in first law analysis, and that

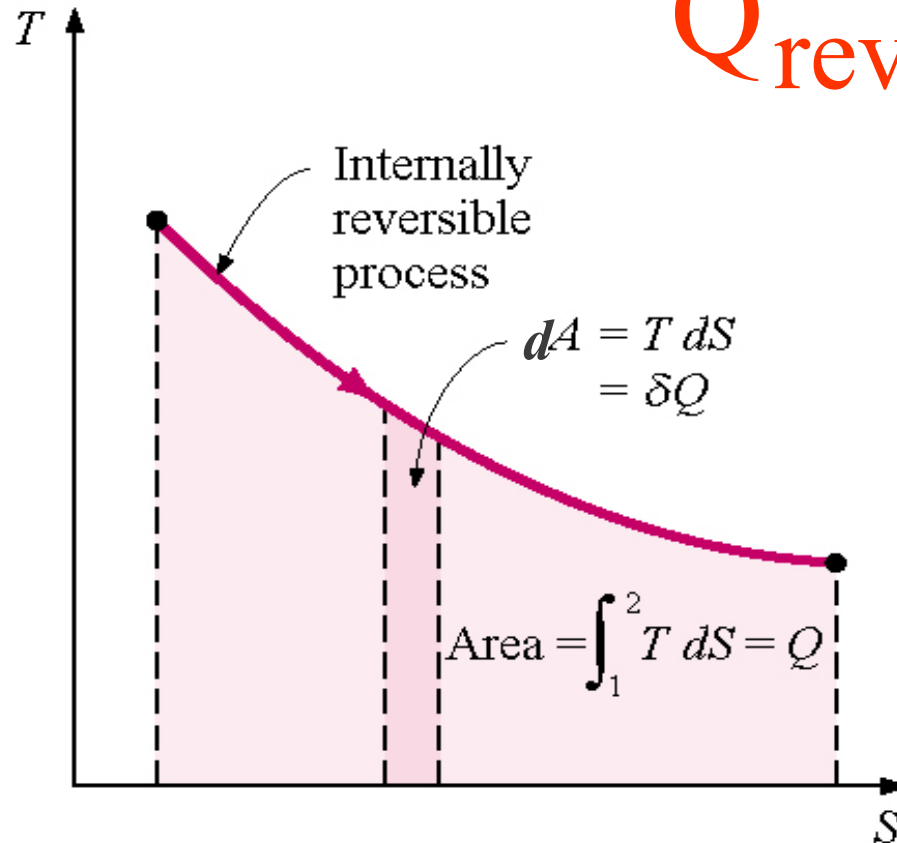
$$w = \int P dv$$

Work was the area under the curve.

Heat Transfer for Internally Reversible Processes

On a T - S diagram, the area under the process curve represents the heat transfer for internally reversible processes

$$Q_{\text{rev}} = \int_1^2 T dS$$



Derivation of Tds equations:

The 1st Law:

$$\delta Q - \delta W = dU$$

The work is given by:

$$\delta W = PdV$$

**For a reversible
process:**

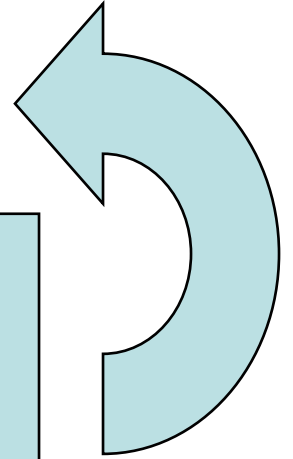
$$TdS = \delta Q$$

Substituting gives:

$$TdS = dU + PdV$$

**Or on a per unit
mass basis:**

$$Tds = du + Pdv$$



Tds Equations

- Entropy is a property.
- The *Tds* expression that we just derived expresses entropy in terms of other properties.
- The properties are independent of path....
- We can use the *Tds* equation we just derived to calculate the entropy change between any two states:

$$***Tds = du + Pdv***$$

Tds Equations

Starting with enthalpy $h = u + Pv$, it is possible to develop a second *Tds* equation:

$$\begin{aligned} dh &= d(u + Pv) \\ &= \underbrace{du + Pdv}_{Tds} + vdP \\ &= Tds + vdP \end{aligned}$$

$$***Tds = dh - vdP***$$

Tds equations

- These **two Tds** relations have many uses in thermodynamics and serve as the starting point in developing entropy-change relations for processes.

$$***Tds = du + Pdv***$$

$$***Tds = dh - vdP***$$

Entropy change of an Pure substance

- The *entropy-change* and *isentropic relations* for a process can be summarized as follows:

1. Pure substances:

Any process: $\Delta s = s_2 - s_1$ [kJ/(kg-K)]

Isentropic process: $s_2 = s_1$

The entropy change for an incompressible substance:

We start with the first Tds equation:

$$Tds = C_v(T) dT + Pdv$$

For incompressible substances, $v \cong \text{const}$, so $dv = 0$.

We also know that $C_v(T) = C(T)$, so we can write:

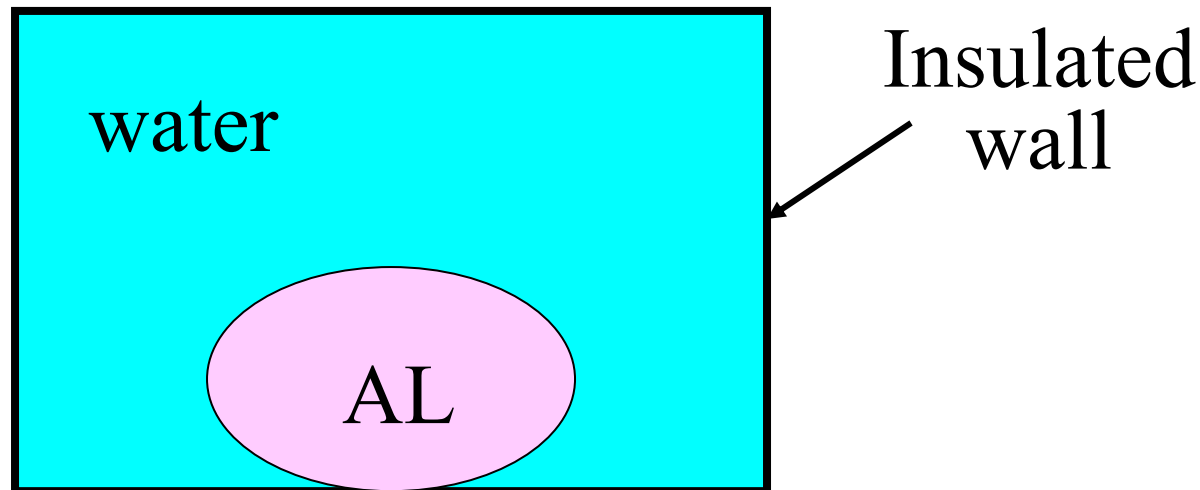
$$ds = [C(T)/T]dT \rightarrow s_2 - s_1 = \int_{T_1}^{T_2} [C(T)/T]dT$$

If the specific heat does not vary with temperature:

$$s_2 - s_1 = C \ln\left(\frac{T_2}{T_1}\right)$$

Sample Problem

Aluminum at 100°C is placed in a large, insulated tank having 10 kg of water at a temperature of 30°C . If the mass of the aluminum is 0.5 kg, find: i) the final temperature of the aluminum and water, ii) the entropy of the aluminum and the water, and iii) the total entropy of the universe due this process.



System including aluminum and water
Constant volume, adiabatic, no work done

Conservation of Energy

Apply the first law

$$\cancel{Q} - \cancel{W} = \Delta U_{\text{sys}} = \Delta U_W + \Delta U_{AL}$$

$$m_W C_W (T_2 - T_1)_W + m_{AL} C_{AL} (T_2 - T_1)_{AL} = 0$$

But $(T_2)_W = (T_2)_{AL} = T_2$ at equilibrium

$$\therefore T_2 = \frac{m_W C_W (T_1)_W + m_{AL} C_{AL} (T_1)_{AL}}{m_W C_W + m_{AL} C_{AL}}$$

Solve for Temperature

$$m_W = 10 \text{ kg}, \quad C_W = 4.177 \text{ kJ/kg}\cdot\text{K}$$

$$m_{AL} = 0.5 \text{ kg}, \quad C_{AL} = 0.941 \text{ kJ/kg}\cdot\text{K}$$

See
Table A-14

$$T_2 = \frac{(10 \text{ kg})(4.177 \frac{\text{kJ}}{\text{kg}\cdot\text{K}})(303 \text{ K}) + (0.5 \text{ kg})(0.941 \frac{\text{kJ}}{\text{kg}\cdot\text{K}})(373 \text{ K})}{(10 \text{ kg})(4.177 \frac{\text{kJ}}{\text{kg}\cdot\text{K}}) + (0.5 \text{ kg})(0.941 \text{ kJ} / \text{kg}\cdot\text{K})}$$

$$T_2 = 303.8 \text{ K}$$

Entropy Transfer

Entropy change for water and aluminum

$$\begin{aligned}\Delta S_W &= m_W C_W \ln \frac{T_2}{T_{1,W}} \\ &= (10 \text{ kg}) \left(4.177 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \right) \ln \left(\frac{303.8 \text{ K}}{303 \text{ K}} \right) = 0.1101 \frac{\text{kJ}}{\text{K}}\end{aligned}$$

$$\begin{aligned}\Delta S_{AL} &= m_{AL} C_{AL} \ln \frac{T_2}{T_{1,AL}} \\ &= (0.5 \text{ kg}) \left(0.941 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \right) \ln \frac{303.8 \text{ K}}{373 \text{ K}} = -0.0966 \frac{\text{kJ}}{\text{K}}\end{aligned}$$

Entropy Generation

Entropy production of the universe

$$\begin{aligned} S_{gen} &= \Delta S_{total} = \Delta S_W + \Delta S_{AL} \\ &= 0.1101 \frac{kJ}{K} - 0.0966 \frac{kJ}{K} \\ &= 0.0135 \frac{kJ}{K} > 0 \end{aligned}$$

$S_{gen} > 0$: irreversible process

The Entropy Change of an Ideal Gas

Entropy Change for an Ideal Gas

Start with 2nd Tds eq. $Tds = dh - v dP$

Remember dh and v for an ideal gas?

$$dh = C_p dT \quad \text{and} \quad v = RT/P$$

Substituting: $Tds = C_p dT - \frac{RT}{P} dP$

Dividing by T
and integrating:

$$s_2 - s_1 = \int_{T_1}^{T_2} C_p(T) \frac{dT}{T} - R \ln \frac{P_2}{P_1}$$

Don't forget, $C_p = C_p(T)$ a function of temperature!

Entropy change of an ideal gas

- Similarly it can be shown from

$$***Tds = du + Pdv***$$

that

$$***s_2 - s_1 = \int_{T_1}^{T_2} C_v(T) \frac{dT}{T} + R \ln \frac{v_2}{v_1}***$$

Entropy change of an ideal gas for constant specific heats: Approximation

- Now, if the temperature range is so limited that $C_p \cong \text{constant}$ (and $C_v \cong \text{constant}$),

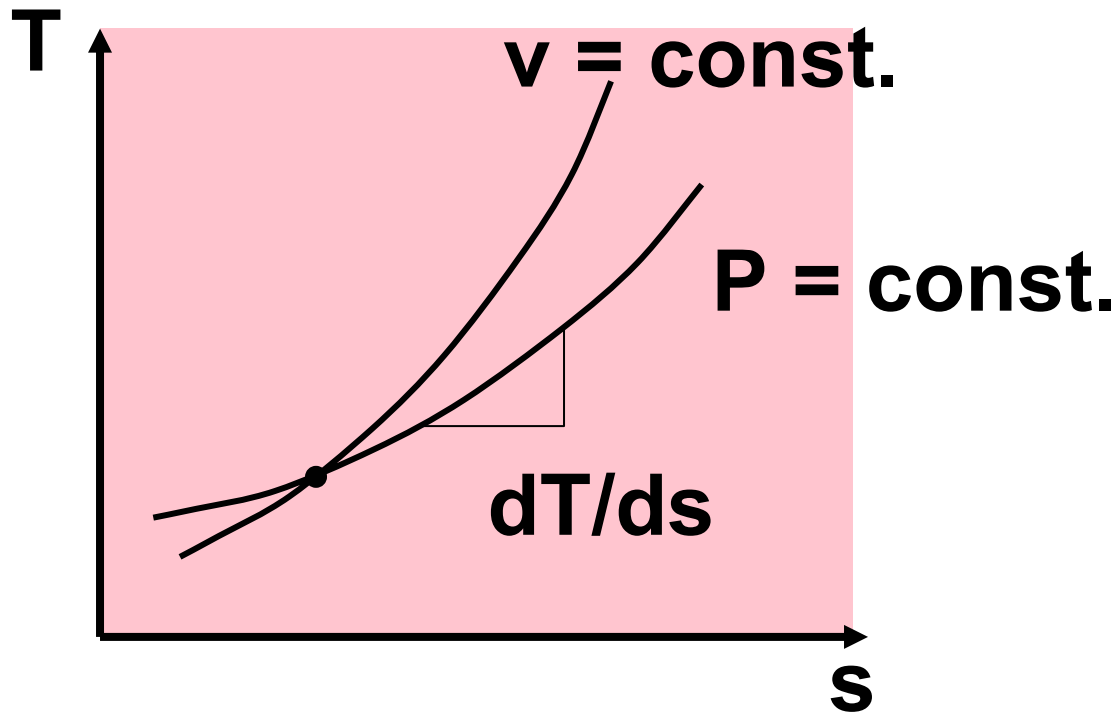
$$s_2 - s_1 = C_{p,\text{av}} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

or

$$s_2 - s_1 = C_{v,\text{av}} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$

**Constant lines of v and P for
Ideal gases diagrams**

$$Tds = du + Pdv \rightarrow v = \text{const} \rightarrow dT/ds|_v = T/C_v$$
$$Tds = dh - vdp \rightarrow P = \text{const} \rightarrow dT/ds|_P = T/C_P$$
$$C_P > C_v \quad \therefore \quad dT/ds|_v > dT/ds|_P$$



Summary: Entropy change of an Pure substance

1. Pure substances:

Any process:

$$\Delta s = s_2 - s_1 \text{ [kJ/(kg-K)] (Table)}$$

Isentropic process:

$$s_2 = s_1$$

Summary: Entropy Change for Incompressible Substance

2. Incompressible substances:

Any process:

$$s_2 - s_1 = C_{av} \ln \frac{T_2}{T_1}$$

Isentropic process: $T_2 = T_1$

Summary: Entropy Change for Ideal gases

3. Ideal gases:

Constant specific heats (approximate treatment):

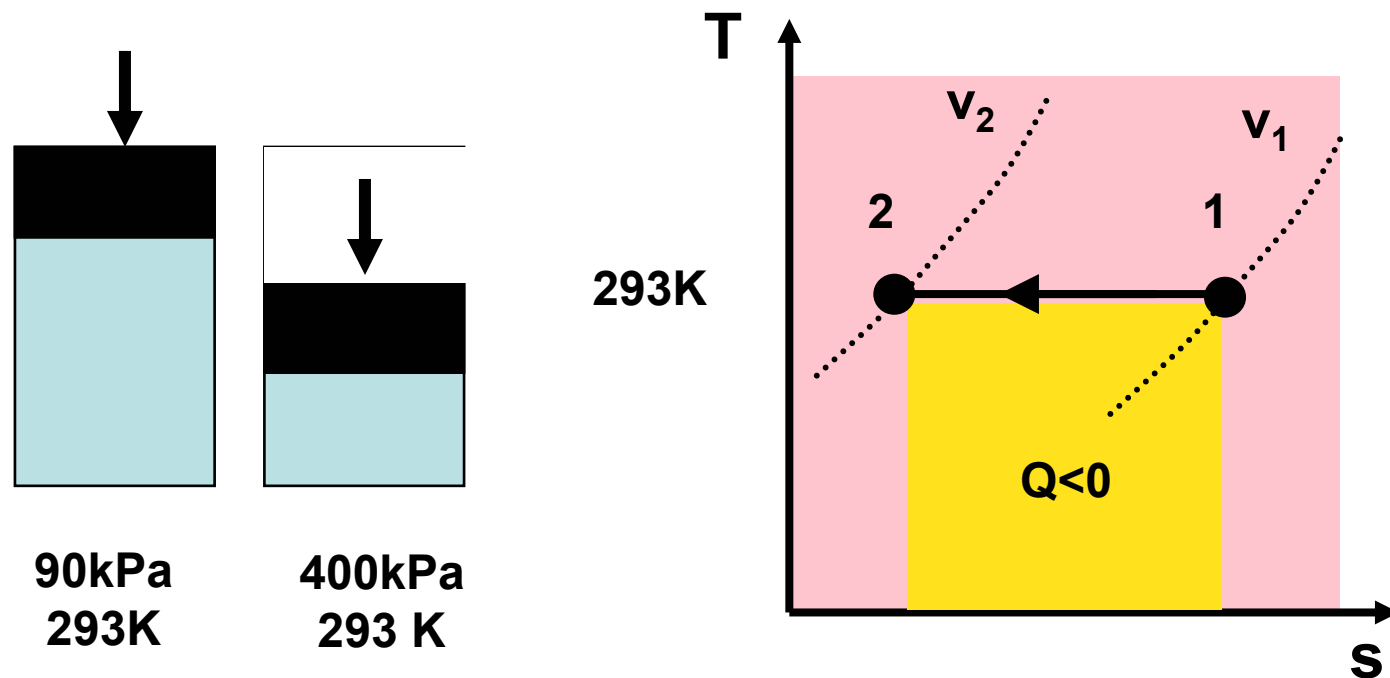
$$s_2 - s_1 = C_{v,av} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \quad [kJ/(kg \cdot K)]$$

$$s_2 - s_1 = C_{p,av} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad [kJ/(kg \cdot K)]$$

Isentropic process: $Pv^k = const$

TEAMPLAY : Air is compressed in a piston-cylinder device from 90 kPa and 20°C to 400 kPa in a reversible isothermal process.

Determine: (a) the entropy change of air, (b) the work done and (c) the removed heat.



Air is ideal gas, $R = 287 \text{ Jkg}^{-1}\text{K}^{-1}$

Entropy change for an ideal gas with constant heat :

$$s_2 - s_1 = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} = -287 \ln \frac{400}{90} = -428 \left(\frac{\text{J}}{\text{kgK}} \right)$$

Ideal gas isothermal compression work:

$$W_{\text{comp}} = -RT \ln \frac{P_2}{P_1} = -287 \cdot 298 \cdot \ln \frac{400}{90} = -125.4 \left(\frac{\text{kJ}}{\text{kg}} \right)$$

Rejected heat (1st law):

$$Q - W_{\text{comp}} = \Delta U \rightarrow Q \equiv W_{\text{comp}} = -125.4 \left(\frac{\text{kJ}}{\text{kg}} \right)$$

Alternatively, for an isothermal *reversible* process:

$$q = T\Delta s = 293 \cdot 0.428 \equiv -125.4 \left(\frac{\text{kJ}}{\text{kg}} \right)$$

- The entropy of the air decreased due to the heat extraction.
- Consider the heat is rejected on the environment at 15°C (288K). Evaluate the entropy change of the environment and the air.

- The environment is a **heat reservoir**. The entropy change is $\Delta s = Q/T = 125400/288 = \underline{+ 435 \text{ JK}^{-1}}$.

- The entropy change of the system plus the environment is therefore:

$$\Delta s = \Delta s_{\text{system}} + \Delta s_{\text{environ}} = - 428 + 435 = 7 \text{ JK}^{-1}.$$

- If the environment is at 20°C, $\Delta s = 0$ because both are at the same temperature (reversible heat transfer).

Sample Problem

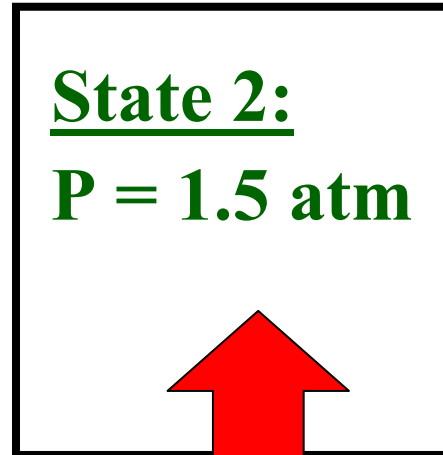
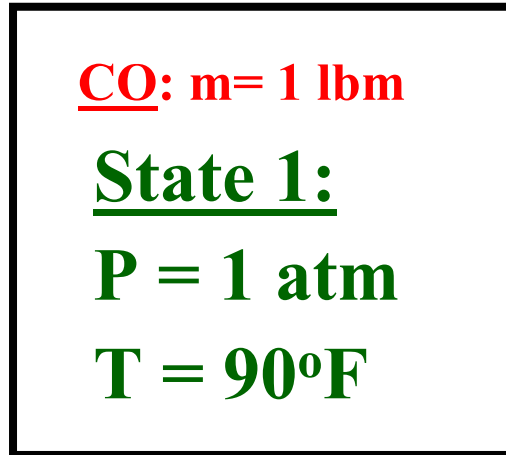
A rigid tank contains 1 lbm of carbon monoxide at 1 atm and 90°F. Heat is added until the pressure reaches 1.5 atm. Compute:

(a) The heat transfer in Btu.

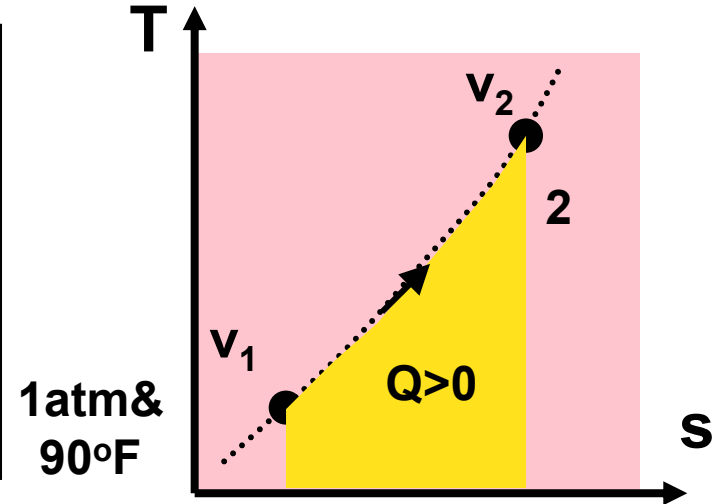
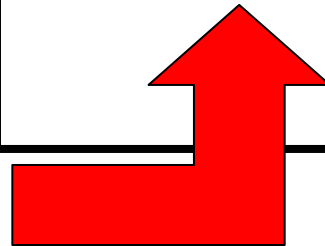
(b) The change in entropy in Btu/R.

Draw diagram:

Rigid Tank \Rightarrow volume is constant

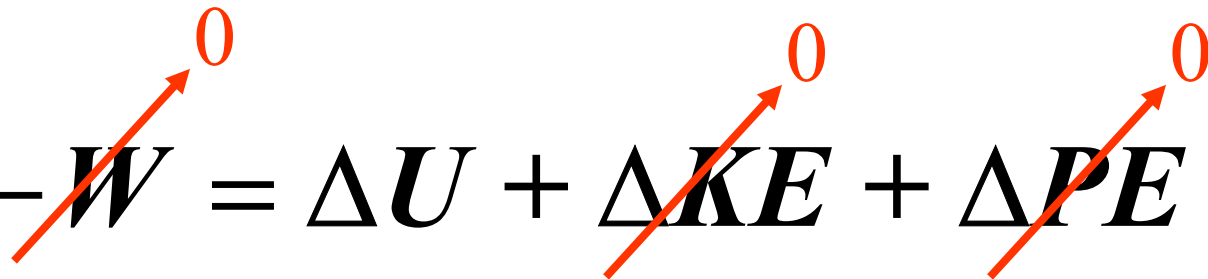


Heat Transfer



- CO in tank is system
- Work is zero- rigid tank
- kinetic energy changes zero
- potential energy changes zero
- CO is ideal gas
- Constant specific heats

Apply assumptions to conservation of energy equation

$$Q - \cancel{W} = \Delta U + \cancel{\Delta KE} + \cancel{\Delta PE}$$


For constant specific heats, we get:

$$Q = mC_v(T_2 - T_1)$$

Need $T_2 \Rightarrow$ How do we get it?

Apply ideal gas equation of state:

$$\frac{P_1 V_1}{P_2 V_2} = \frac{mRT_1}{mRT_2}$$

Cancel common terms...

Solve for T_2 :

$$T_2 = \left(\frac{P_2}{P_1} \right) T_1 = \left(\frac{1.5}{1.0} \right) (90 + 460) R = 825 R$$

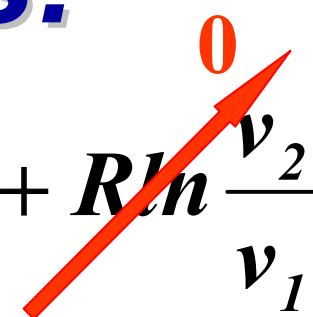
Solve for heat transfer

$$Q = (1 \text{ lbm}) \left(0.18 \frac{\text{Btu}}{\text{lbm R}} \right) (825 - 550) \text{ R}$$

$$Q = 49.5 \text{ Btu}$$

Now, let's get entropy change ...

For constant specific heats:

$$S_2 - S_1 = m \left(C_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \right)$$


Since $v_2 = v_1$ $S_2 - S_1 = m C_v \ln \frac{T_2}{T_1}$

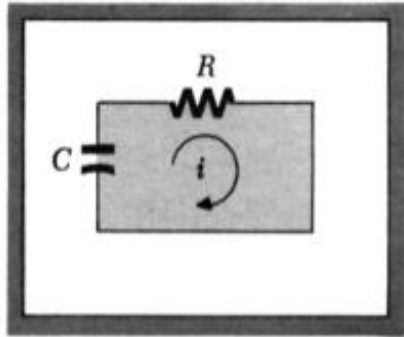
$$S_2 - S_1 = (1 \text{ lbm}) \left(0.18 \frac{\text{Btu}}{\text{lbm R}} \right) \ln \left(\frac{825 \text{ R}}{550 \text{ R}} \right)$$

$$S_2 - S_1 = 0.073 \text{ Btu/R}$$

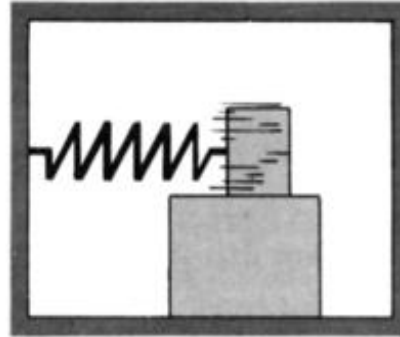
Entropy Change in Some Selected Irreversible Processes

Some Irreversible Processes

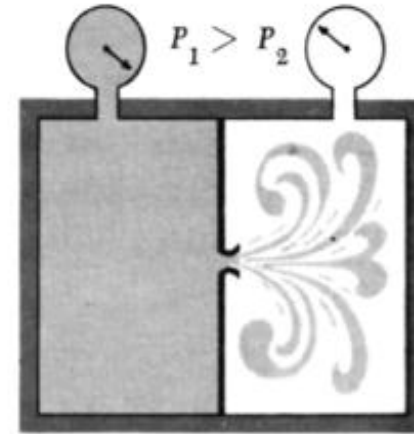
ONE WAY PROCESSES



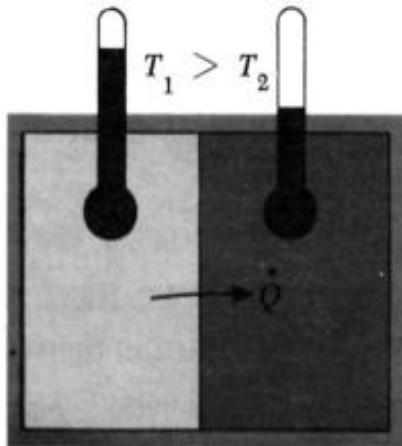
(a) *Current flow through a resistance*



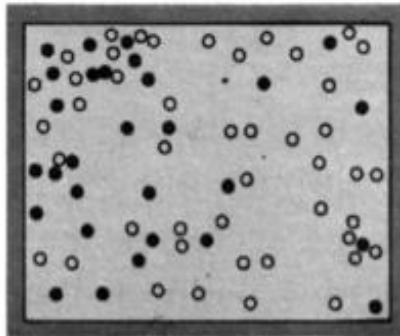
(b) *Motion with friction*



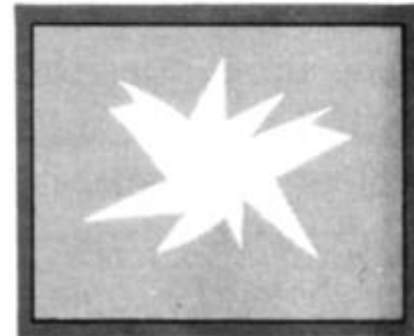
(c) *Unrestrained expansion*



(d) *Energy transfer as heat*

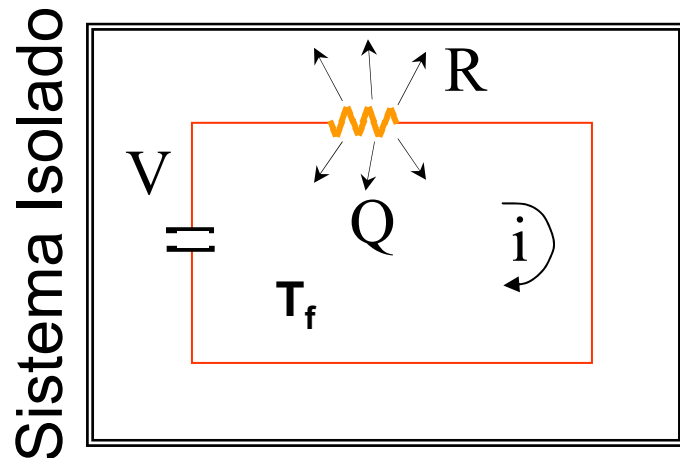


(e) *Diffusion*



(f) *Spontaneous chemical reaction*

PROCESSOS IRREVERSÍVEIS: EFEITO JOULE



Sistema Isolado- não há calor cruzando a fronteira e todo trabalho é transformado em energia interna:

$$U_f - U_i = Ri \cdot [t_f - t_i] \quad (1a.lei)$$

$$S_f - S_i = \int_i^f \frac{\delta Q}{T} + P_s \quad (2a.lei)$$

Todo trabalho elétrico é convertido em energia interna do sistema. A variação de S é devido a P_s , pois $\delta Q=0$.

Como S não depende do caminho,

$$T_f dS = dU = Ri \Delta t \quad \rightarrow P_s = Ri \Delta t / T_f > 0.$$

Trabalho elétrico convertido em energia interna aumentou a entropia do sistema isolado. Não é possível converter a mesma quantidade de energia interna em trabalho elétrico.

PROCESSOS IRREVERSÍVEIS: EFEITO JOULE

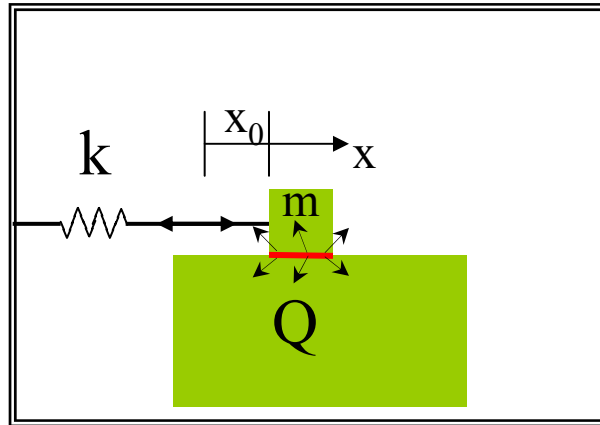
Por que não é possível converter a mesma quantidade de energia interna em trabalho elétrico?

Do ponto de vista microscópico: o sistema deveria resfriar para diminuir a energia interna e transformá-la em energia elétrica. Certamente este não será o estado mais provável de encontrá-lo portanto, esta transformação não será espontânea!

Do ponto de vista macroscópico a entropia do sistema isolado deveria diminuir e isto violaria a 2ª Lei! Note que de (i) - \rightarrow (f), $\Delta S > 0$

PROCESSOS IRREVERSÍVEIS: ATRITO

Sistema Isolado



Sistema Isolado- não há calor cruzando a fronteira e toda energia Potencial da mola é transformada em energia interna:

$$U_f - U_i = k \cdot x_0^2 \quad (1a.lei)$$

$$S_f - S_i = \int_i^f \delta Q/T + P_s \quad (2a.lei)$$

Toda energ. pot. mola é convertida em energia interna do sistema. A variação de S é devido a P_s , pois $\delta Q=0$.

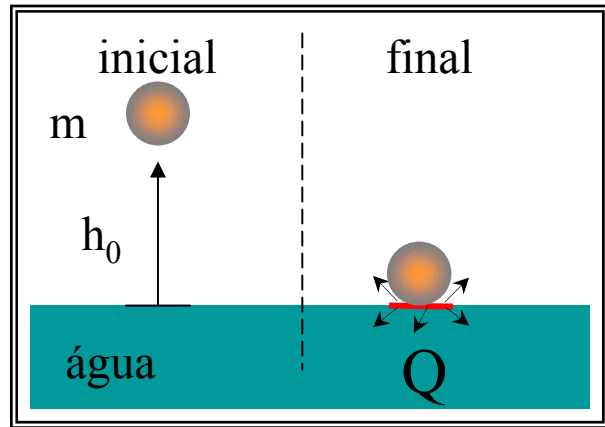
Como S não depende do caminho,

$$TdS = dU = (1/2)kx_0^2 - \rightarrow P_s = (1/2)kx_0^2 / T > 0 \text{ \& } S_f > S_i.$$

Aumentou a entropia do sistema isolado. Não é possível converter a mesma quantidade de energia interna em energia potencial da mola!

PROCESSOS IRREVERSÍVEIS: QUEDA LIVRE

Sistema Isolado



Sistema Isolado- não há calor cruzando a fronteira e toda energia Potencial é transformada em energia interna após choque com água

$$U_f - U_i = m \cdot g \cdot h_0 \quad (1a.lei)$$

$$S_f - S_i = \int_i^f \delta Q/T + P_s \quad (2a.lei)$$

Toda energ. pot. é convertida em energia interna do sistema. A variação de S é devido a P_s , pois $\delta Q=0$.

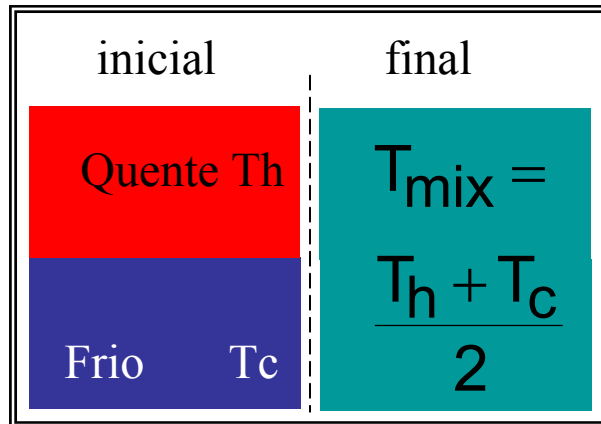
Como S não depende do caminho,

$$TdS = dU = mgh_0 - \rightarrow P_s = mgh_0 / T > 0 \quad \& \quad S_f > S_i.$$

Aumentou a entropia do sistema isolado. Não é possível converter a mesma quantidade de energia interna para elevar a bola na posição inicial h_0 !

PROCESSOS IRREVERSÍVEIS: DIFERENÇA TEMP.

Sistema Isolado



Sistema Isolado- energia interna permanece constante (blocos com mesma massa e calor específico porém a T_h e T_c)

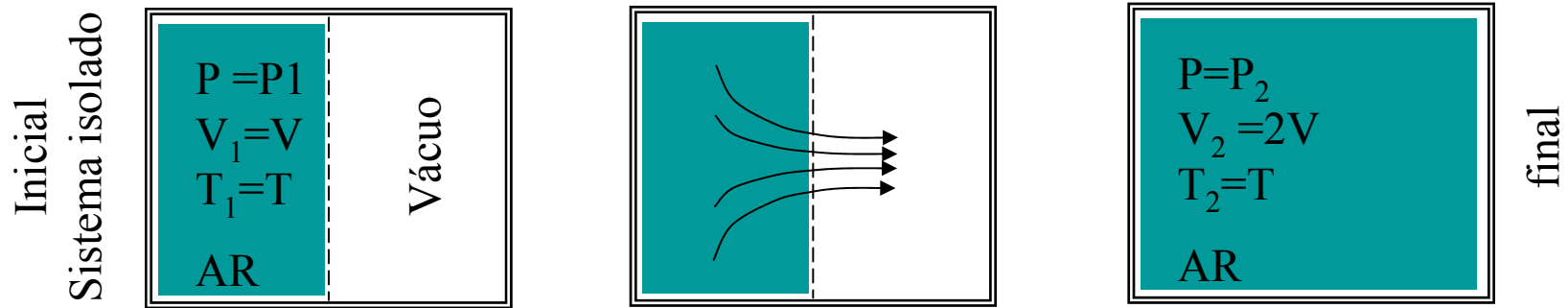
$$U_q = U_q + U_f \rightarrow T_{mix} = \frac{T_q + T_f}{2} \quad (1a.lei)$$

$$\Delta S = C \ln\left(\frac{T_{mix}}{T_c}\right) + C \ln\left(\frac{T_h}{T_{mix}}\right) \equiv C \ln\left(\frac{T_h}{T_c}\right) > 0 \text{ pq. } T_q > T_f \quad (2a.lei)$$

S do sistema isolado é considerado como a soma de S do sistema quente e frio. S_{quente} diminui mas S_{frio} aumenta de modo que a variação total é maior que zero.

Troca de calor com diferença de temperatura é irreversível. O bloco que atinge T_{mix} não volta espontaneamente para T_h e T_c , é necessário trabalho!

PROCESSOS IRREVERSÍVEIS: EXPANSÃO COM DIFERENÇA DE PRESSÃO



Sistema Isolado- ➤ na expansão para o vácuo não há calor nem trabalho cruzando a fronteira. A energia interna do gás permanece a mesma. $T_1 = T_2$ (1ª lei)

Processo isotérmico: $P_1 V_1 = P_2 V_2$ ou $P_2 = 0.5 P_1$

Variação da Entropia:

$$TdS = \underbrace{dU}_{=0} + PdV \rightarrow dS = \frac{PdV}{T} = MR \frac{dV}{V} \rightarrow \Delta S = MRLN \left[\frac{V_2}{V_1} \right] > 0$$

Durante a expansão contra o vácuo a capacidade de realizar trabalho do gás foi perdida (não havia máq. p/ extrair trabalho). A transf. inversa é irreversível pois $\Delta S > 0$

Isentropic Process

For a reversible, adiabatic process

$$\delta Q_{\text{REV}} = 0 \Rightarrow dS = 0 \quad \text{or} \quad S_2 = S_1$$

For an ideal gas $\rightarrow ds=0$ and $v dP = C_p dT$

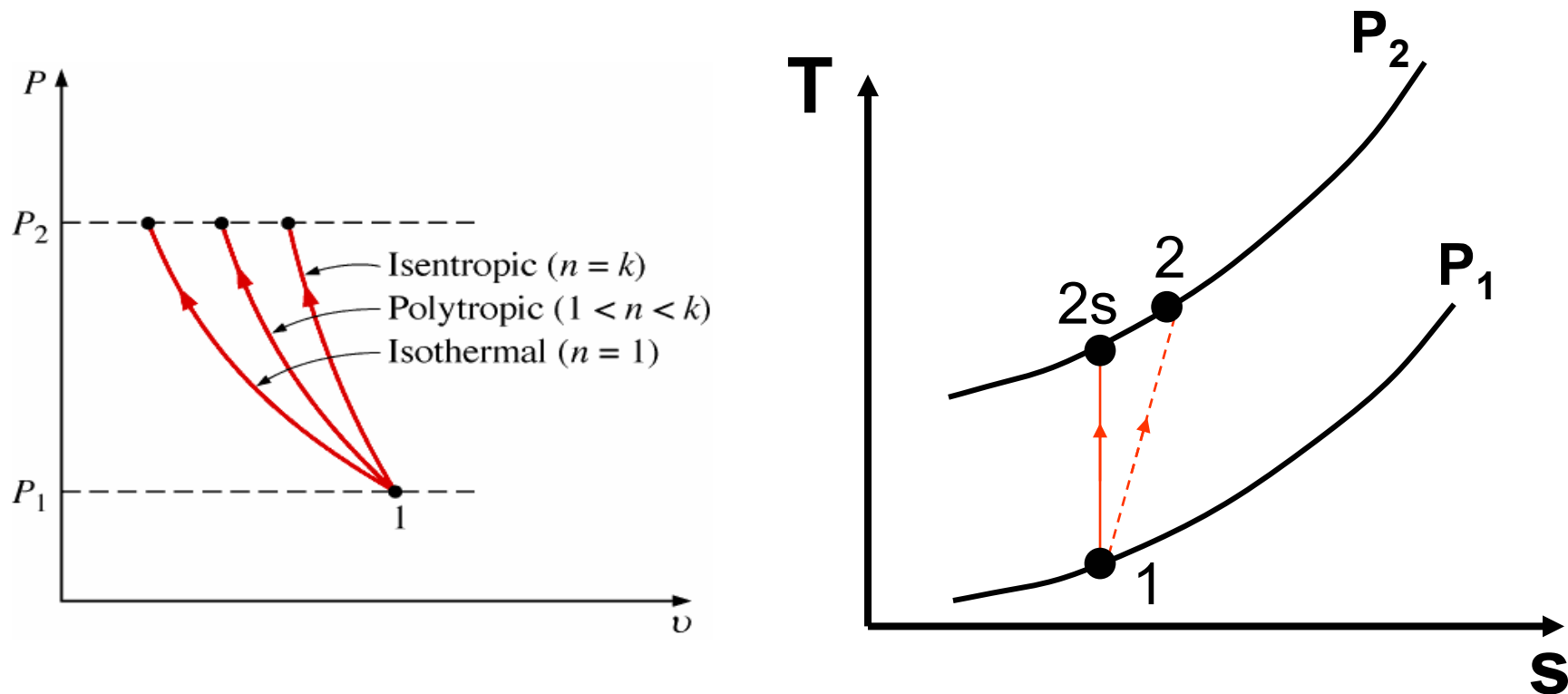
Using $v = RT/P$ and the fact that $R = C_p - C_v$,

$$(C_p - C_v) \frac{dP}{P} = C_p \frac{dT}{T} \Rightarrow \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{T_2}{T_1} \right)$$

Recovers the adiabatic and reversible ideal gas relations, $Pv^\gamma = \text{const.}$

Adiabatic Process: Reversible x Irreversible

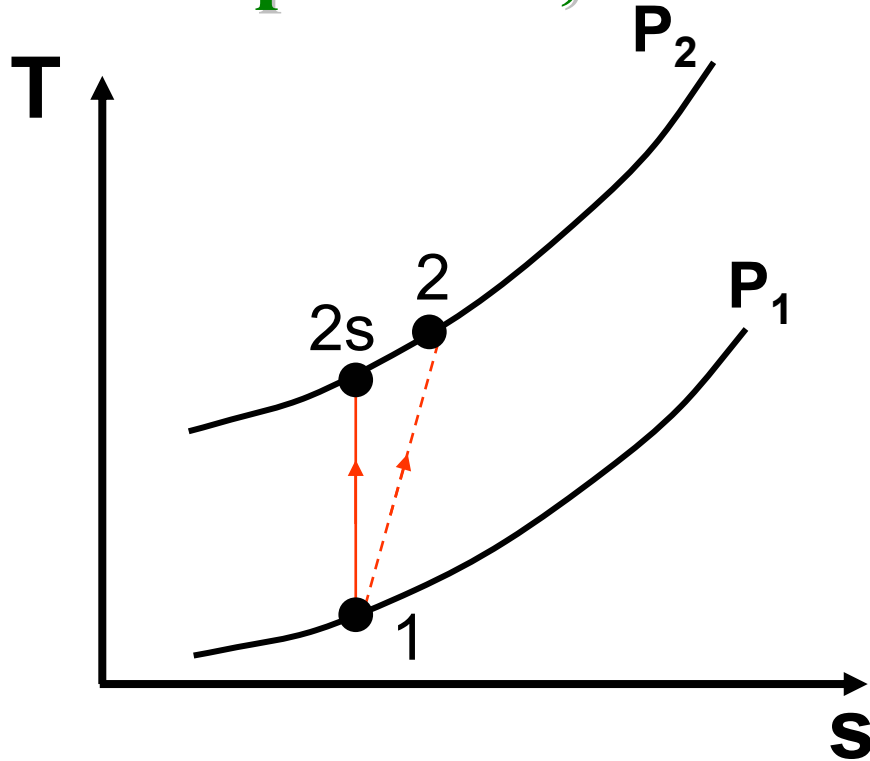
$$\delta Q = 0 \Rightarrow dS \geq 0 \quad \text{or} \quad P_S \geq 0$$



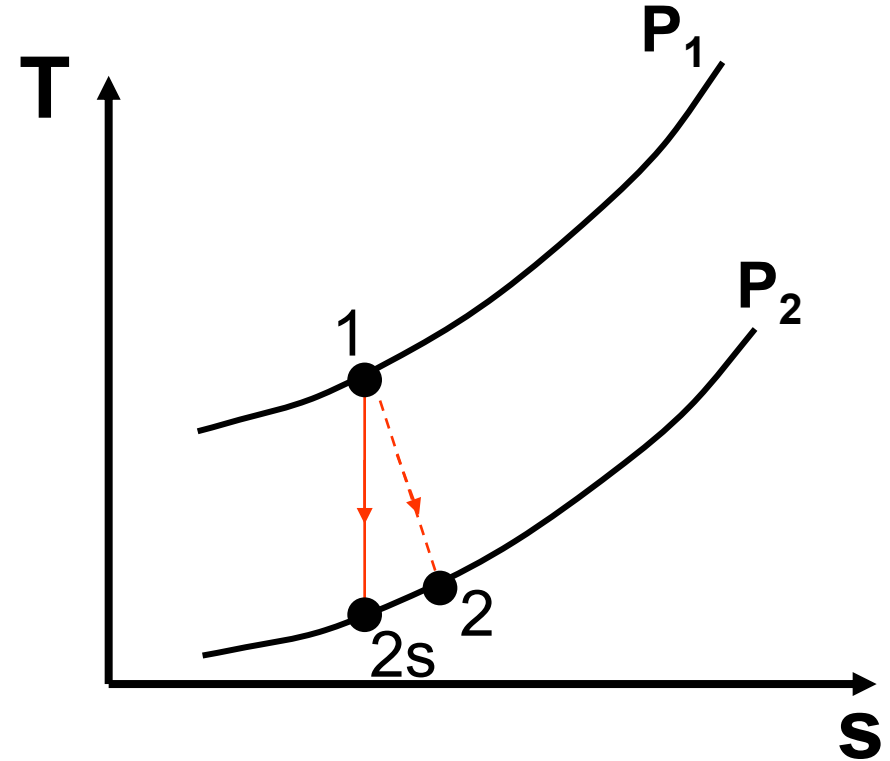
For an adiabatic process (1→2) ΔS is constant or greater than zero due to entropy generation.

Adiabatic Process: Reversible x Irreversible

Compression, $W < 0$



Expansion, $W > 0$



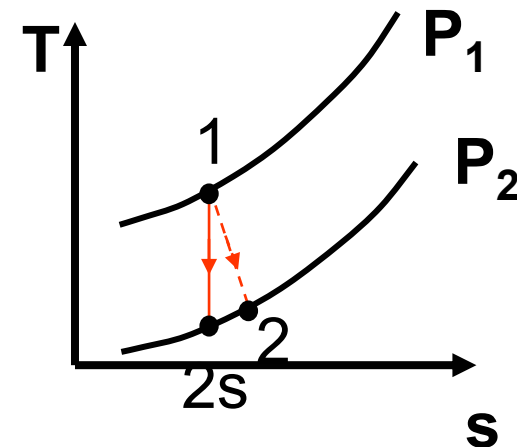
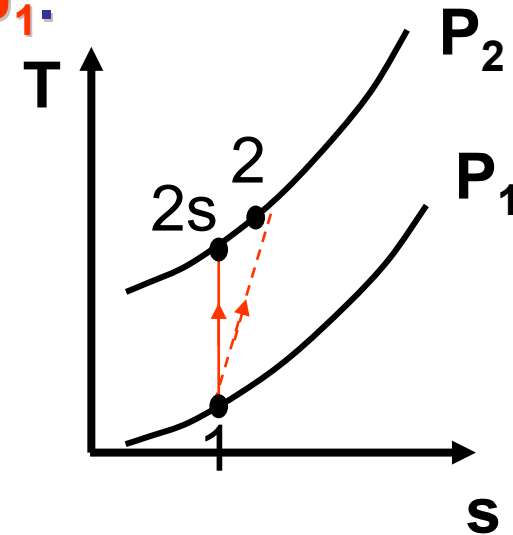
ΔS is constant or greater than zero due to entropy generation independent if it is an adiabatic expansion or compression.

Available Work in an Adiabatic Process: Reversible x Irreversible

The first law states for an adiabatic process that $W = U_2 - U_1$.

For compression, $T_{2s} < T_2$,
since $U \sim T$, then the
reversible process requires
less work than the
irreversible, i.e., $W_{REV} < W$.

For expansion, $T_{2s} > T_2$,
since $U \sim T$, then the
reversible process delivers
more work than the
irreversible, i.e., $W_{REV} > W$.



Process Efficiency

A reversible process may have an increase or decrease of Entropy but **THERE IS NO ENTROPY GENERATION.**

An actual process which does or receive work is often compared against an ideal reversible process.

The process efficiency is often taken as the ratio between the actual work and the ideal reversible work.

Available Work in a Process: Reversible x Irreversible Paths

The 1st and 2nd law
combined result →
eliminating dQ →

$$\delta Q = dU + \delta W_{\text{REAL}}$$

$$TdS = \delta Q + \delta I_{\text{irr}}$$

$$PdV - \delta I_{\text{irr}} = \delta W_{\text{REAL}}$$

but PdV is a reversible work mode, then

$$\delta W_{\text{REV}} - \delta I_{\text{irr}} = \delta W_{\text{REAL}} \rightarrow \delta W_{\text{REV}} - \delta W_{\text{REAL}} = \delta I_{\text{irr}} > 0$$

or

$$1 - \frac{W_{\text{REAL}}}{W_{\text{REV}}} \geq 0 \rightarrow \eta \leq 1$$

the work delivered in a reversible process is
always equal or greater than the one in a
irreversible process.

Available Work in a Process: Reversible x Irreversible Path

Either for compression or expansion, the irreversibilities :

- 1. increase the system entropy due to the entropy generation by the irreversibilities,**
- 2. a fraction of the available work is spent to overcome the irreversibilities which in turn increase the internal energy,**

What For Are the Reversible Process?

- They are useful for establishing references between actual and 'ideal' processes.
- The process efficiency defined as the ratio of the work delivered by an actual and a reversible process compares how close they are.

$$\eta = \frac{W_{\text{actual}}}{W_{\text{reversible}}}$$

- It must not be confused the process efficiency with the thermal eff. of heat engines! The latter operates in a cycle.

TEAMPLAY

Um carro com uma potência de 90 kW tem uma eficiência térmica de 30%. Determine a taxa de consumo de combustível se o poder calorífico do mesmo é de 44.000 kJ/kg. Considere a densidade do combustível de 800g/l

1. Energia consumida = $90/0.3 = 300$ kJ/s
2. Massa de combustível = $300/44000 = 6.818 \cdot 10^{-3}$ kg/s
3. Volume combustível ($\rho = 800\text{g/l}$) = $8.523 \cdot 10^{-3}$ l/s
4. A potência máxima se a velocidade média do carro for de 140km/h ($3.89 \cdot 10^{-3}$ km/s) então o consumo de combustível será de: 4.56 Km/l

Recommended Exercises

4-18 4-19 4-23 4-25

4.26 4-34

TEAMPLAY

A 50-kg iron block and a 20-kg copper block, both initially at 80°C, are dropped into a large lake at 15°C. Thermal equilibrium is established after a while as a result of heat transfer between the blocks and the lake water. Determine the total entropy generation for this process.