$T - ds$ relations

Entropy change for a process can be evaluated by integrating δQ/T along some imaginary internally reversible path between the actual end states

From energy equation for a closed stationary system (a reversible process)

$$\delta Q_{int\ rev} - \delta W_{int\ rev,out} = dU$$

$$\delta Q_{int\ rev} = TdS \quad \text{and} \quad \delta W_{int\ rev,out} = PdV$$

Thus

$$\boxed{TdS = dU + PdV}$$

Called Gibbs equation

Or per unit mass

$$\boxed{Tds = du + Pdv}$$

From the definition of enthalpy

$$h = u + Pv \rightarrow dh = du + Pdv + vdP$$

$$Tds = \left(dh - Pdv - vdP\right) + Pdv$$

Thus

$$\boxed{Tds = dh - vdP}$$

Entropy change of liquids and solids

Entropy equation

(valid in both reversible and irreversible processes)

$$\boxed{Tds = du + Pdv}$$

For ideal gas $du = C_v dT \quad and \quad dh = C_p dT$

For incompressible substance

(specific volume remains constant) $\longrightarrow$

$$dv \cong 0$$

$$C_p = C_v = C$$

$$\boxed{ds = \frac{du}{T} = \frac{CdT}{T}}$$

Entropy change of solid or liquid

$$\boxed{s_2 - s_1 = \int_1^2 C(T)\frac{dT}{T} \cong C_{av} \ln\frac{T_2}{T_1}}$$

where C_{av} = average specific heat of substance over the given temperature

Entropy change of liquids and solids

For an isentropic process $\Delta s = 0$

$$s_2 - s_1 = C_{av} \ln \frac{T_2}{T_1} = 0 \longrightarrow T_2 = T_1$$

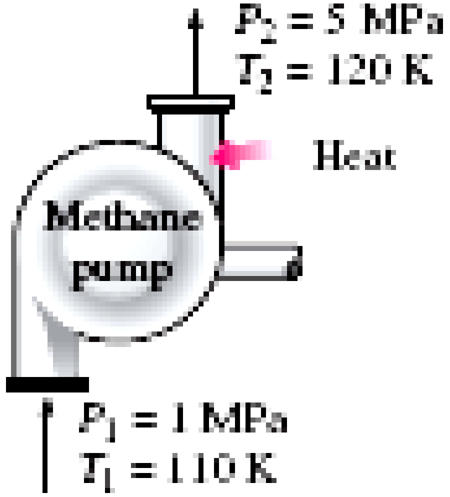
This means that temperature is constant $\longrightarrow$ **Isothermal process**

Example: effect of density of a liquid on entropy

Liquid methane is commonly used in various cryogenic applications. The critical temperature of methane is 191 K (or 82°C), and thus methane must be maintained below 191 K to keep it in liquid phase. The properties of liquid methane at various temperatures and pressures are given in Table. Determine the entropy change of liquid methane as it undergoes a process from 110 K and 1 MPa to 120 K and 5 MPa

(a) using tabulated properties and

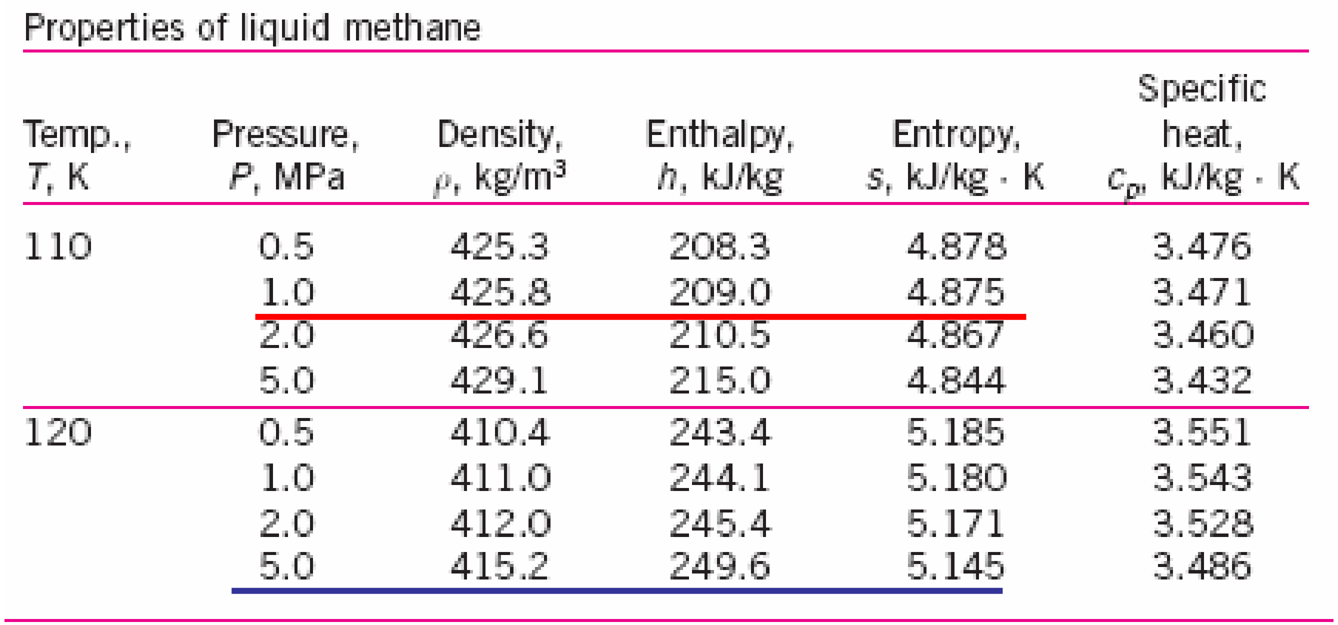
(b) approximating liquid methane as an incompressible substance. What is the error involved in the latter case?



Example: effect of density of a liquid on entropy

(a) Find entropy from actual data

- ❑ **From following Table**



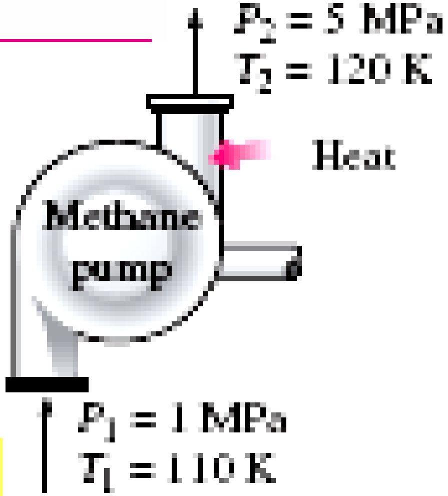
Properties of liquid methane

Temp., T, K	Pressure, P, MPa	Density, ρ, kg/m^3	Enthalpy, h, kJ/kg	Entropy, s, kJ/kg · K	Specific heat, c_p, kJ/kg · K
110	0.5	425.3	208.3	4.878	3.476
	1.0	425.8	209.0	4.875	3.471
	2.0	426.6	210.5	4.867	3.460
	5.0	429.1	215.0	4.844	3.432
120	0.5	410.4	243.4	5.185	3.551
	1.0	411.0	244.1	5.180	3.543
	2.0	412.0	245.4	5.171	3.528
	5.0	415.2	249.6	5.145	3.486

State 1 $\left.\begin{array}{l} P_1 = 1 \quad \text{MPa} \\ T_1 = 110 \quad \text{K} \end{array}\right\} \quad \begin{array}{l} s_1 = 4.875 \quad \text{kJ/kg.K} \\ C_{p,1} = 3.471 \quad \text{kJ/kg.K} \end{array}$

State 2 $\left.\begin{array}{l} P_2 = 5 \quad \text{MPa} \\ T_2 = 120 \quad \text{K} \end{array}\right\} \quad \begin{array}{l} s_2 = 5.145 \quad \text{kJ/kg.K} \\ C_{p,2} = 3.486 \quad \text{kJ/kg.K} \end{array}$

$$\Delta s = s_2 - s_1 = 5.145 - 4.875 = 0.27 \text{ kJ/kg.K}$$



Example: effect of density of a liquid on entropy

(b) Find entropy from approximation assuming methane to be incompressible

$$\boxed{s_2 - s_1 = \int_1^2 C(T)\frac{dT}{T} \cong C_{av}\ln\frac{T_2}{T_1}}$$

$$C_{p,ave} = \frac{C_{p,1}+C_{p,2}}{2} = \frac{3.471+3.486}{2} = 3.7485\ \text{kJ/kg.K}$$

Thus

$$\Delta s = (3.4785)\ln\frac{120}{110} = 0.303\ \ \text{kJ/kg.K}$$

$$Error = \frac{\left|\Delta s_{actual} - \Delta s_{ideal}\right|}{\Delta s_{actual}} = \frac{\left|0.27 - 0.303\right|}{0.27} = 0.122 \quad (12.2\%)$$

Due to the change of density of liquid methane!

Entropy change of ideal gas

$$Tds = du + Pdv$$

$$ds = \frac{du}{T} + \frac{Pdv}{T} \quad = C_v \frac{dT}{T} + R\frac{dv}{v}$$

where for Ideal gas $u = C_v dT$ and Pv = RT

Thus entropy change

$$\boxed{s_2 - s_1 = \left\{\int_1^2 C_v(T)\frac{dT}{T}\right\} + R\ln\frac{v_2}{v_1}}$$

$$Tds = dh - vdP$$

$$ds = \frac{dh}{T} - \frac{vdP}{T} \quad = C_p \frac{dT}{T} - \frac{RdP}{P}$$

where for Ideal gas $h = C_p dT$ and Pv = RT

Thus entropy change

$$\boxed{s_2 - s_1 = \left\{\int_1^2 C_p(T)\frac{dT}{T}\right\} - R\ln\frac{P_2}{P_1}}$$

Entropy change of ideal gas (cont.)

Entropy change

$$s_2 - s_1 = \left\{ \int_1^2 C_v(T)\frac{dT}{T} \right\} + R\ln\frac{v_2}{v_1}$$

$$s_2 - s_1 = \left\{ \int_1^2 C_p(T)\frac{dT}{T} \right\} - R\ln\frac{P_2}{P_1}$$

For constant specific heat, $C_{p,1\text{-}2} = C_{p,av}$ and $C_{v,1\text{-}2} = C_{v,av}$

⇓

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

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

Acceptable when temperature change is small

Isentropic process of ideal gas (cont.)

For constant specific heat

(a)

$$s_2 - s_1 = 0 \rightarrow \quad C_{v,av} \ln \frac{T_2}{T_1} = -R \ln \frac{v_2}{v_1}$$

$$\ln \frac{T_2}{T_1} = \ln \left(\frac{v_1}{v_2} \right)^{\frac{R}{C_v}} \longrightarrow \boxed{\frac{T_2}{T_1} = \left(\frac{v_1}{v_2} \right)^{k-1}}$$

$$R = C_p - C_v$$

$$k = C_p / C_v$$

(b)

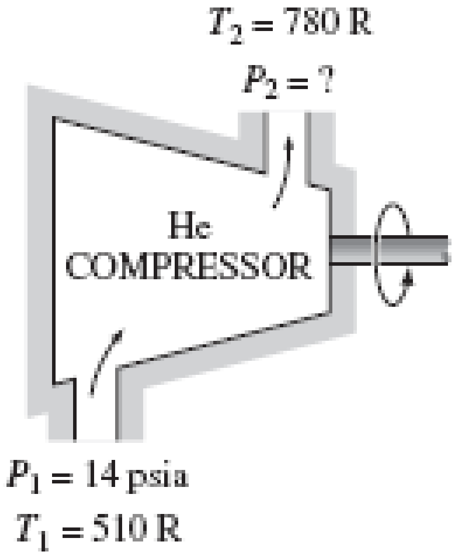
$$s_2 - s_1 = 0 \rightarrow \quad C_{p,av} \ln \frac{T_2}{T_1} = R \ln \frac{P_2}{P_1}$$

$$\ln \frac{T_2}{T_1} = \ln \left(\frac{P_2}{P_1} \right)^{\frac{R}{C_p}} \longrightarrow \boxed{\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}}}$$

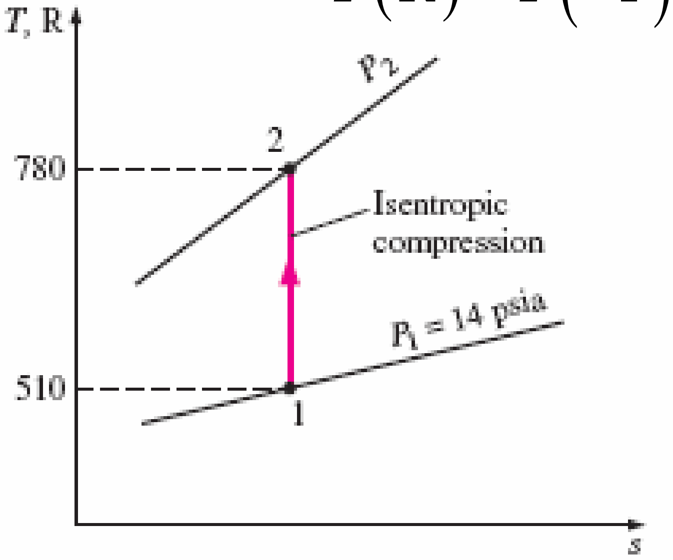
$$\boxed{\frac{P_2}{P_1} = \left(\frac{v_1}{v_2} \right)^{k}}$$

Example: isentropic compression of an ideal gas

Helium gas is compressed by an adiabatic compressor from an initial state of 14 psia and 50°F to a final temperature of 320°F in a reversible manner. Determine the exit pressure of helium. Specific heat ratio k of helium is 1.667

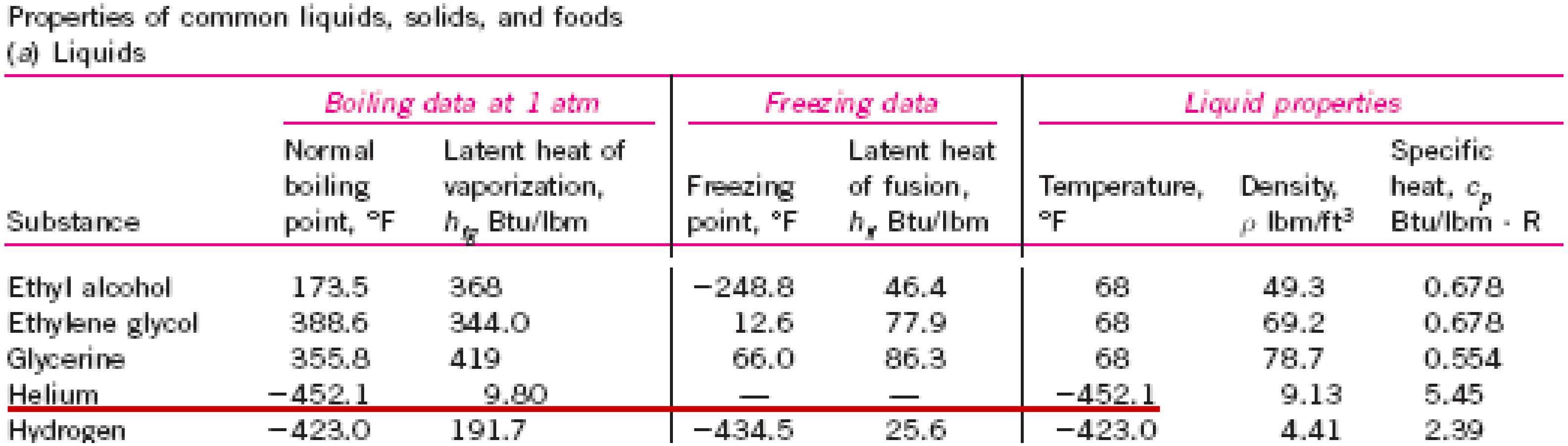


$$T(\mathrm{R}) = T(^{\mathrm{O}}\mathrm{F}) + 459.67$$



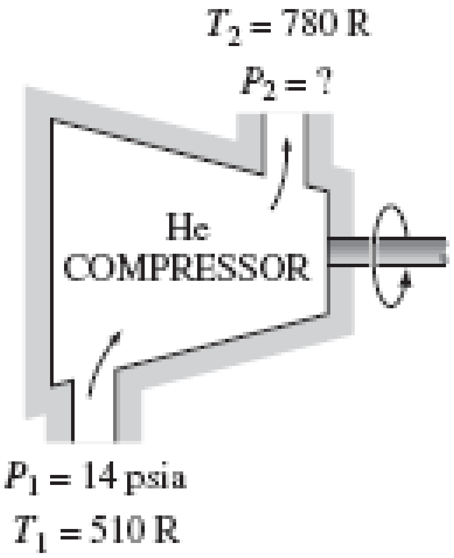
Example: isentropic compression of an ideal gas

Since helium is at high temperature relative to its critical point value of -450°F, helium can be treated as an ideal gas



Properties of common liquids, solids, and foods
(*a*) Liquids

	Boiling data at 1 atm		*Freezing data*		*Liquid properties*		
Substance	Normal boiling point, °F	Latent heat of vaporization, h_{fg} Btu/lbm	Freezing point, °F	Latent heat of fusion, h_{if} Btu/lbm	Temperature, °F	Density, ρ lbm/ft³	Specific heat, c_p Btu/lbm · R
Ethyl alcohol	173.5	368	−248.8	46.4	68	49.3	0.678
Ethylene glycol	388.6	344.0	12.6	77.9	68	69.2	0.678
Glycerine	355.8	419	66.0	86.3	68	78.7	0.554
Helium	−452.1	9.80	—	—	−452.1	9.13	5.45
Hydrogen	−423.0	191.7	−434.5	25.6	−423.0	4.41	2.39



$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}$$

$$P_2 = P_1\left(\frac{P_2}{P_1}\right)^{\frac{k}{k-1}} = (14\ \text{psia})\left(\frac{780\ R}{510\ R}\right)^{\frac{1.667}{1.667-1}} = 40.5\ \text{psia}$$

Example

Air initially at 0.1 MPa, 27°C, is compressed reversibly to a final state.

(a) Find the entropy change of the air when the final state is 0.5 MPa, 227°C.

(b) Find the entropy change when the final state is 0.5 MPa, 180°C.

(c) Find the temperature at 0.5 MPa that makes the entropy change zero.

Assume air is an ideal gas with constant specific heats.

a.

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

$$= 1.005 \frac{kJ}{kg \cdot K} \ln\left(\frac{(227+273)K}{(27+273)K}\right) - 0.287 \frac{kJ}{kg \cdot K} \ln\left(\frac{0.5\,MPa}{0.1\,MPa}\right)$$

$$= +0.0507 \frac{kJ}{kg \cdot K}$$

b.

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

$$= 1.005 \frac{kJ}{kg \cdot K} \ln\left(\frac{(180+273)K}{(27+273)K}\right) - 0.287 \frac{kJ}{kg \cdot K} \ln\left(\frac{0.5\,MPa}{0.1\,MPa}\right)$$

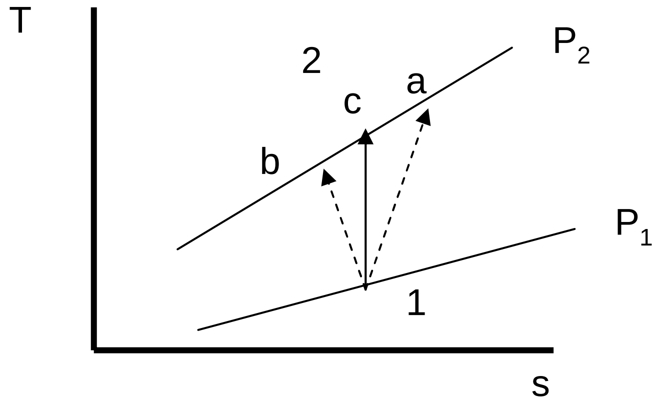
$$= -0.0484 \frac{kJ}{kg \cdot K}$$

Example

(c) Find the temperature at 0.5 MPa that makes the entropy change zero.

$$
\begin{aligned}
T_2 &= T_1\left(\frac{P_2}{P_1}\right)^{(k-1)/k} \\
&= (27+273)K\left(\frac{0.5\,MPa}{0.1\,MPa}\right)^{(1.4-1)/1.4} \\
&= 475.4K = 202.4^{o}\,C
\end{aligned}
$$

The *T-s* plot is



Reversible Steady-Flow Work

Isentropic, Steady Flow through Turbines, Pumps, and Compressors

Consider a turbine, pump, compressor, or other steady-flow control volume, work-producing device.

The general first law for the steady-flow control volume is

$$\dot{E}_{in} = \dot{E}_{out}$$

$$\dot{Q}_{net} + \sum_{inlets} \dot{m}_i \left(h_i + \frac{\vec{V}_i^{\,2}}{2} + gz_i\right) = \dot{W}_{net} + \sum_{exits} \dot{m}_e \left(h_e + \frac{\vec{V}_e^{\,2}}{2} + gz_e\right)$$

For a one-entrance, one-exit device undergoing an internally reversible process, this general equation of the conservation of energy reduces to, on a unit of mass basis

$$\delta w_{rev} = \delta q_{rev} - dh - dke - dpe$$

where $\delta q_{rev} = T\,ds$

$$\delta w_{rev} = T\,ds - dh - dke - dp$$

Reversible Steady-Flow Work

Using the Gibb’s second equation, this becomes

$$dh = T\,ds + v\,dP$$

$$\delta w_{rev} = -v\,dP - dke - dpe$$

Integrating over the process, this becomes

$$w_{rev} = -\int_1^2 v\,dP - \Delta ke - \Delta pe \qquad \left(\frac{kJ}{kg}\right)$$

Neglecting changes in kinetic and potential energies, reversible work becomes

$$w_{rev} = -\int_1^2 v\,dP \qquad \left(\frac{kJ}{kg}\right)$$

Based on the classical sign convention, this is the work **done by** the control volume. When work is done on the control volume such as compressors or pumps, the reversible work going **into** the control volume is

Reversible work input $$w_{rev,\,in} = \int_1^2 v\,dP + \Delta ke + \Delta pe \qquad \left(\frac{kJ}{kg}\right)$$

Reversible Steady-Flow Work

$$w_{rev,\,in} = \int_1^2 v\,dP + \Delta ke + \Delta pe \qquad \left(\frac{kJ}{kg}\right)$$

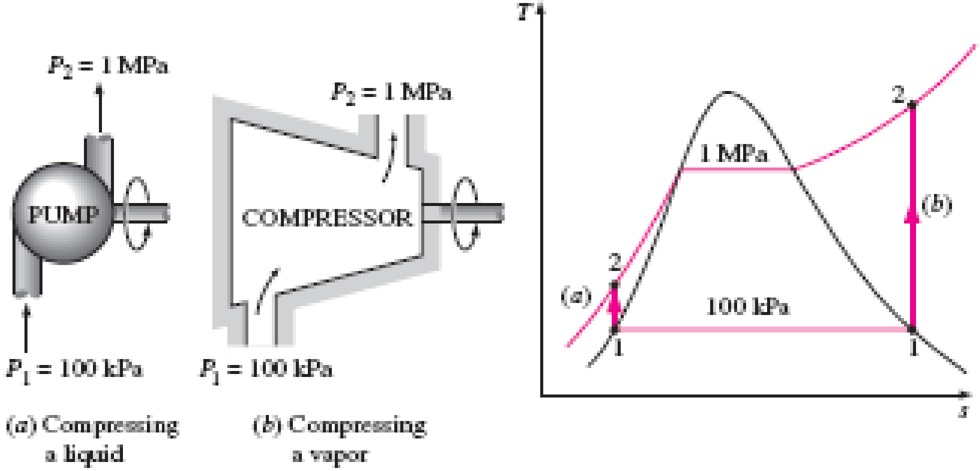
$$= v\Delta P + \Delta ke + \Delta pe$$

For the steady-flow of an incompressible fluid through a device that involves **no work interactions** (**such as nozzles or a pipe section**), the work term is zero, and the equation above can be expressed as the well-know **Bernoulli equation** in fluid mechanics.

$$v(P_2 - P_1) + \Delta ke + \Delta pe = 0$$

Example

Determine the compressor work input required to compress steam isentropically from 100 kPa to 1 MPa, assuming that the steam exists as (a) saturated liquid and (b) saturated vapor at the inlet state.



(a) Compressing a liquid

(b) Compressing a vapor

Assumptions

1. Steady operating condition
2. Neglect PE and KE
3. Isentropic process

(a) Steam is a saturated liquid initially $\longrightarrow v_1 = v_{f\,@100\,\text{kPa}} = 0.001043\ \text{m}^3/\text{kg}$

$$w_{rev,in} = \int_1^2 v\,dP \cong v_1\left(P_2 - P_1\right)$$

$$= \left(0.001043\ \text{m}^3/\text{kg}\right)\left(1000 - 100\ \text{kPa}\right)\frac{1\ \text{kJ}}{1\ \text{kPa.m}^3} = 0.94\ \frac{\text{kJ}}{\text{kg}}$$

Example

(b) From information pressure changes from 100 kPa to 1 MPa

Thus v varies with P

$Tds = dh - vdP$ But for a isentropic process $dh = vdP$

Thus

$$w_{rev,in} = \int_1^2 vdP = \int_1^2 dh = h_2 - h_1$$

State 1 $\left.\begin{matrix} P_1 = 100 \quad \text{kPa} \\ (sat.vapor) \end{matrix}\right\}$ $\begin{matrix} h_1 = 2675.5 \quad \text{kJ/kg} \\ s_1 = 7.3594 \ \text{kJ/kg.K} \end{matrix}$ From table

State 2 $\left.\begin{matrix} P_2 = 1 \quad \text{MPa} \\ s_2 = s_1 \end{matrix}\right\} h_2 = 3195.5 \quad \text{kJ/kg}$ From table

$$w_{rev,in} = 3195.5 - 2675.5 = 520 \quad \text{kJ/kg}$$

Example

Saturated liquid water at 10 kPa leaves the condenser of a steam power plant and is pumped to the boiler pressure of 5 MPa. Calculate the work for an isentropic pumping process.

a. Work for the reversible process can be applied to the isentropic process

$$\dot{W}_C = \dot{m} v_1 (P_2 - P_1)$$

Here at 10 kPa, $v_1 = v_f$ = 0.001010 m3/kg.

The work per unit mass flow is

$$w_C = \frac{\dot{W}_C}{\dot{m}} = v_1 (P_2 - P_1)$$

$$= 0.001010 \frac{m^3}{kg} (5000 - 10) kPa \frac{kJ}{m^3 kPa}$$

$$= 5.04 \frac{kJ}{kg}$$

Example

b. Using the steam table data for the isentropic process, we have

$$-\dot{W}_{net} = \dot{m}(h_2 - h_1)$$

$$-(0 - \dot{W}_C) = \dot{m}(h_2 - h_1)$$

From the saturation pressure table,

$$\left.\begin{array}{l} P_1 = 10\,kPa \\ Sat.\ Liquid \end{array}\right\} \left\{\begin{array}{l} h_1 = 191.81\dfrac{kJ}{kg} \\ s_1 = 0.6492\dfrac{kJ}{kg \cdot K} \end{array}\right.$$

Since the process is isentropic, $s_2 = s_1$. Interpolation in the compressed liquid tables gives

$$\left.\begin{array}{l} P_2 = 5\,MPa \\ s_2 = s_1 = 0.6492\dfrac{kJ}{kg \cdot K} \end{array}\right\} h_2 = 197.42\dfrac{kJ}{kg}$$

Example

The work per unit mass flow is

$$w_C = \frac{\dot{W}_C}{\dot{m}} = (h_2 - h_1)$$

$$= (197.42 - 191.81)\frac{kJ}{kg}$$

$$= 5.61\frac{kJ}{kg}$$

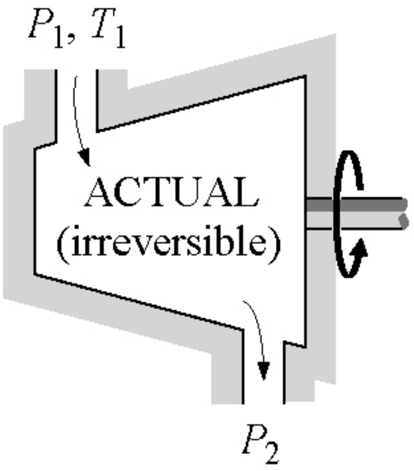
Isentropic or adiabatic efficiencies

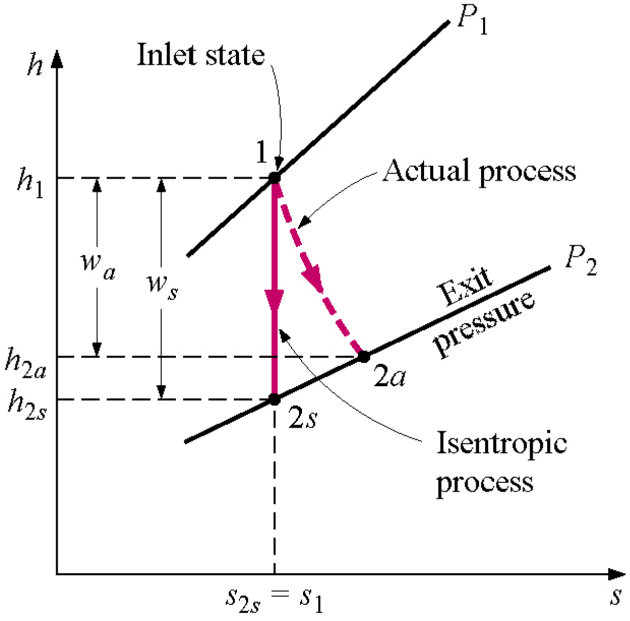
Most steady-flow devices operate under adiabatic conditions, and the ideal process for these devices is the isentropic process.

Isentropic device

- Turbine,
- Compressor or Pump
- Nozzle

Turbine





The isentropic work is the maximum possible work output that the adiabatic turbine can produce; therefore, the actual work is less than the isentropic work. Since efficiencies are defined to be less than 1, the turbine isentropic efficiency is defined as

$$\boxed{\eta_T = \frac{Actual\ turbine\ work}{Isentropic\ turbine\ work} = \frac{w_a}{w_s}}$$

$$\eta_T \cong \frac{h_1 - h_{2a}}{h_1 - h_{2s}}$$

Example

The isentropic work of the turbine in is 1152.2 kJ/kg. If the isentropic efficiency of the turbine is 90 percent, calculate the actual work. Find the actual turbine exit temperature or quality of the steam.

Steam enters the turbine at 1 MPa, 600^{o}C, and expands to 0.01 MPa.

$$\eta_T = \frac{Actual\ turbine\ work}{Isentropic\ turbine\ work} = \frac{w_a}{w_s}$$

$$w_a = \eta_T w_s = (0.9)(1153.0\frac{kJ}{kg}) = 1037.7\frac{kJ}{kg}$$

$$\eta_T \cong \frac{h_1 - h_{2a}}{h_1 - h_{2s}}$$

Example

From the steam tables at state 1

$$\left.\begin{array}{l} P_1 = 1 MPa \\ T_1 = 600^o C \end{array}\right\} \left\{\begin{array}{l} h_1 = 3698.6 \dfrac{kJ}{kg} \\ s_1 = 8.0311 \dfrac{kJ}{kg \cdot K} \end{array}\right.$$

At the end of the isentropic expansion process

$$\left.\begin{array}{l} P_2 = 0.01 MPa \\ s_{2s} = s_1 = 8.0311 \dfrac{kJ}{kg \cdot K} \end{array}\right\} \left\{\begin{array}{l} h_{2s} = 2545.6 \dfrac{kJ}{kg} \\ x_{2s} = 0.984 \end{array}\right.$$

The actual turbine work per unit mass flow is

$$w_a = h_1 - h_{2a}$$

$$h_{2a} = h_1 - w_a = (3698.6 - 1037.7) \frac{kJ}{kg} = 2660.9 \frac{kJ}{kg}$$

Example (cont.)

For the actual turbine exit state 2a, the computer software gives

$$\left.\begin{array}{l} P_2 = 0.01\ MPa \\ h_{2a} = 2660.9\,\dfrac{kJ}{kg} \end{array}\right\}\left\{\begin{array}{l} T_{2a} = 86.85^o\,C \\ Superheated \end{array}\right.$$

A second method for finding the actual state 2 comes directly from the expression for the turbine isentropic efficiency. Solve for h_2a.

$$\begin{aligned} h_{2a} &= h_1 - \eta_T\,(h_1 - h_{2s}) \\ &= 3698.6\,\frac{kJ}{kg} - (0.9)(3698.6 - 2545.6)\,\frac{kJ}{kg} \\ &= 2660.9\,\frac{kJ}{kg} \end{aligned}$$

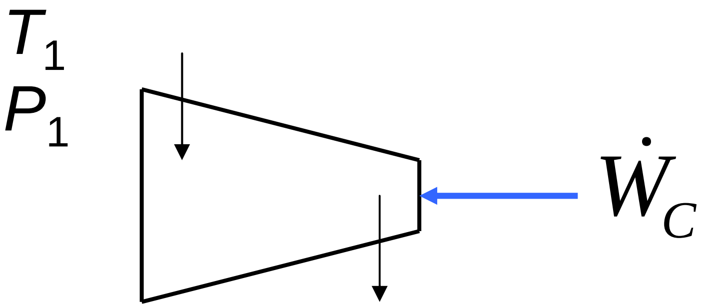
Then P_2 and h_2a give T_2a = 86.85^{o}C.

Compressor and Pump:

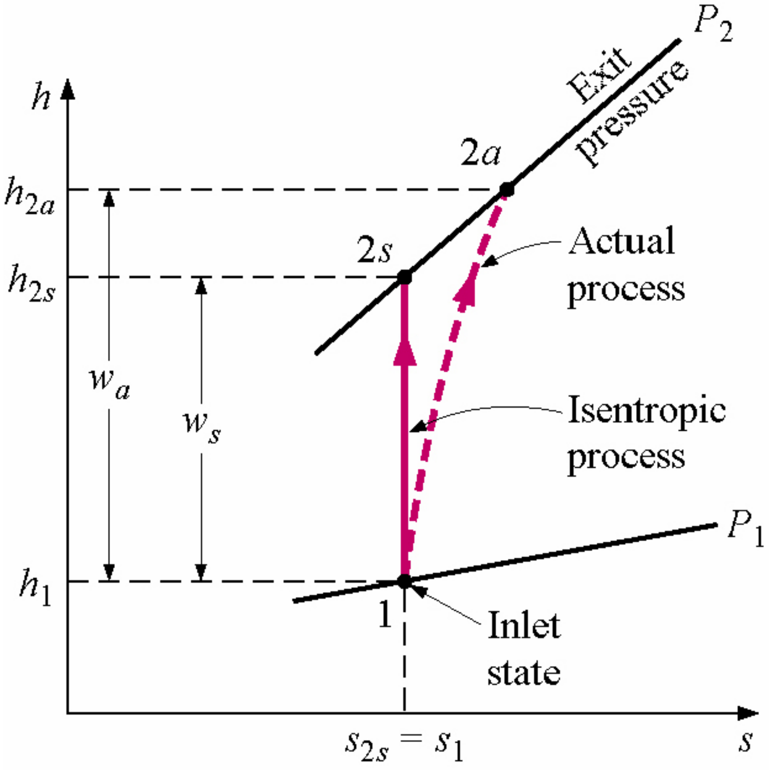
The isentropic work is the minimum possible work that the adiabatic compressor requires; therefore, the actual work is greater than the isentropic work. Since efficiencies are defined to be less than 1, the compressor isentropic efficiency is defined as

$$\boxed{\eta_C = \frac{Isentropic\ compressor\ work}{Actual\ compressor\ work} = \frac{w_s}{w_a}}$$

$$\eta_C \cong \frac{h_{2s} - h_1}{h_{2a} - h_1}$$

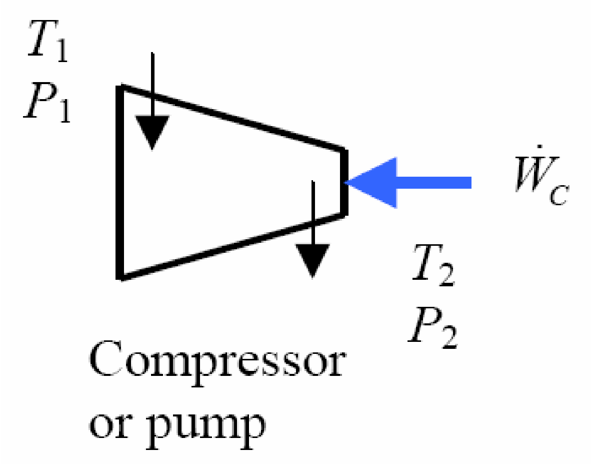


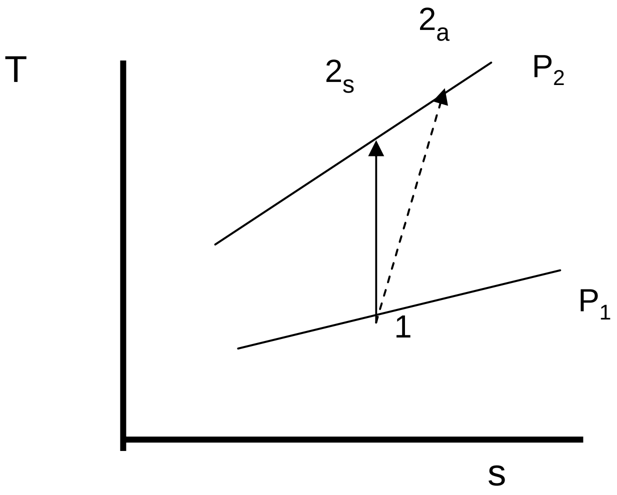
Compressor
or pump



Example

Air enters a compressor and is compressed adiabatically from 0.1 MPa, 27°C, to a final state of 0.5 MPa. Find the work done on the air for a compressor isentropic efficiency of 80 percent.





Ideal gas equations, assume constant properties.

Assume isentropic, steady-flow and then apply the compressor isentropic efficiency to find the actual work.

Example (cont.)

Conservation Principles:

For the isentropic case, $Q_{\text{net}} = 0$. Assuming steady-state, steady-flow, and neglecting changes in kinetic and potential energies for one entrance, one exit, the first law is

$$\dot{E}_{in} = \dot{E}_{out}$$

$$\dot{m}_1 h_1 + \dot{W}_{Cs} = \dot{m}_2 h_{2s}$$

The conservation of mass gives

$$\dot{m}_1 = \dot{m}_2 = \dot{m}$$

The conservation of energy reduces to

$$\dot{W}_{Cs} = \dot{m}(h_{2s} - h_1)$$

$$w_{Cs} = \frac{\dot{W}_{Cs}}{\dot{m}} = (h_{2s} - h_1)$$

Using the ideal gas assumption with constant specific heats, the isentropic work per unit mass flow is

$$w_{Cs} = C_p(T_{2s} - T_1)$$

Example (cont.)

The isentropic temperature at state 2 is found from the isentropic relation

$$T_{2s}=T_1\left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}$$

$$=\left(27+273\,\mathrm{K}\right)\left(\frac{0.5\,\mathrm{MPa}}{0.1}\right)^{\frac{1.4\text{-}1}{1.4}}=475.4\,\mathrm{K}$$

The conservation of energy becomes

$$w_{Cs}=C_p(T_{2s}-T_1)$$

$$=1.005\frac{kJ}{kg\cdot K}(475.4-300)K=176.0\,\frac{kJ}{kg}$$

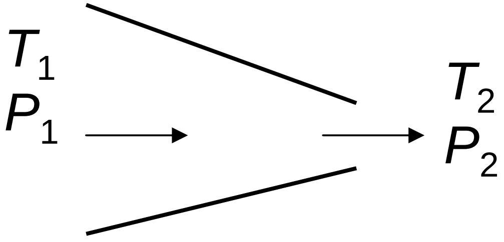
The compressor isentropic efficiency is defined as

$$\eta_C=\frac{w_s}{w_a}\quad\longrightarrow\quad w_{Ca}=\frac{w_{cs}}{\eta_C}=\frac{176\,\frac{kJ}{kg}}{0.8}=220\,\frac{kJ}{kg}$$

Nozzle:

The isentropic kinetic energy at the nozzle exit is the maximum possible kinetic energy at the nozzle exit; therefore, the actual kinetic energy at the nozzle exit is less than the isentropic value. Since efficiencies are defined to be less than 1, the nozzle isentropic efficiency is defined as

$$\boxed{\eta_N = \frac{Actual\ \ KE\ \ at\ \ nozzle\ \ exit}{Isentropic\ \ KE\ \ at\ \ nozzle\ \ exit} = \frac{\vec{V}_{2a}^{2}/2}{\vec{V}_{2s}^{2}/2}}$$



Nozzle