Topic 14
The Tds Relations

Objectives

- Calculate the entropy changes that take place during processes for pure substances, incompressible substances, and ideal gases.

- Examine a special class of idealized processes, called *isentropic processes*, and develop the property relations for these processes.

The T ds Relations

Recall the energy balance:

$$\Delta U = Q - W$$

Now let's apply this for an internally reversible process and let's look at the differential form of the equation:

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

Previously we established that:

$$\delta Q_{int,rev} = TdS$$

And recall that boundary work is:

$$\delta W_{int,rev,out} = PdV$$

The T ds Relations

Now substitute those two equations back into the energy balance equation yields

$$dU = TdS - PdV$$

$$TdS = dU + PdV$$

$$Tds = du + Pd\nu$$

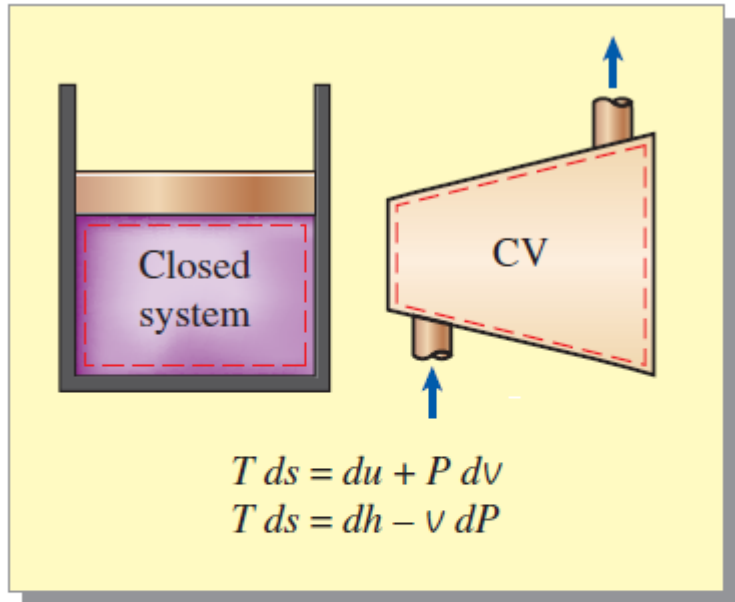Recall what enthalpy is:

$$h = u + P\nu$$

$$dh = du + d(P\nu) = du + \nu dP + Pd\nu$$

$$dh - \nu dP = du + Pd\nu$$

This can then be substituted into the *Tds* equation we just derived.

$$Tds = dh - \nu dP$$

The T ds Relations

FIGURE 7–27

The $T\,ds$ relations are valid for both reversible and irreversible processes and for both closed and open systems.

The first Tds relation: (<u>Gibbs Equation</u>)

$$T\,ds = du + P\,d\nu$$

The second Tds relation:

$$T\,ds = dh - \nu\,dP$$

We can solve for ds in both equations:

$$ds = \frac{du}{T} + \frac{P\,d\nu}{T}$$

$$ds = \frac{dh}{T} - \frac{\nu\,dP}{T}$$

ENTROPY CHANGE OF LIQUIDS AND SOLIDS

Recall liquids and solids are incompressible substances.

$$d\nu \cong 0$$

$$ds = \frac{du}{T} + \frac{Pd\nu}{T}$$

Liquids and solids can be approximated as *incompressible substances* since their specific volumes remain nearly constant during a process.

Recall specific heat equations:

$$du = cdT$$

For liquids and solids $c_p = c_v = c$

$$ds = \frac{du}{T} = \frac{cdT}{T}$$

Entropy Changes of Liquids and Solids

Let's assume that the specific heat is constant and represents an average value of the temperature range we are looking at:

$$ds = \frac{du}{T} = \frac{cdT}{T}$$

$$\int_1^2 ds = \int_1^2 c(T)\frac{dT}{T} \cong c_{avg} \int_1^2 \frac{dT}{T}$$

$$\Delta s = s_2 - s_1 = c_{avg} ln \left(\frac{T_2}{T_1}\right)$$

What if the process is isentropic?

$$\Delta s = 0 = ln \left(\frac{T_2}{T_1}\right)$$

$$T_1 = T_2$$

For solids and liquids, an isentropic process is also <u>isothermal</u>.

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 and must be maintained below this temperature to remain in the liquid phase. Methane enters a pump at 110 K and 1 MPa and leaves at 120 K and 5 MPa. Determine the entropy change during this process by (a) using the table below and (b) using the *Tds* relations.

Properties of Liquid Methane					
Temp	Pressure	Density	Enthalpy	Entropy	Specific Heat
T, K	P, MPa	ρ, kg/m^3	h, kJ/kg	s, kJ/kg K	c_p, kJ/kg K
110	0.5	425.3	208.3	4.878	3.476
	1	425.8	209.0	4.875	3.471
	2	426.6	210.5	4.867	3.460
	5	429.1	215.0	4.844	3.432
120	0.5	410.4	243.4	5.185	3.551
	1	411.0	244.1	5.180	3.543
	2	412.0	245.4	5.171	3.528
	5	415.2	249.6	5.145	3.486

Example 1

Economics of Replacing a Valve by a Turbine

A cryogenic manufacturer handles liquid methane at 115 K and 5 MPa at a rate of 0.280 m³/s. The process involves dropping the pressure to 1 MPa by means of a throttling valve. An engineer proposes to replace the throttling valve with a turbine so power can be produced from the pressure drop. What is the maximum amount of power that can be produced by the turbine? Given that the turbine operates 8760 h/yr and the cost of electricity is $0.075/kWh, what is the maximum savings for the company if they use the turbine?

Example 2

THE ENTROPY CHANGE OF IDEAL GASES

$$ds = \frac{du}{T} + \frac{Pd\nu}{T}$$

Recall Ideal Gas Equation:

$$P = \frac{RT}{\nu}$$

$$\Delta s = s_2 - s_1 = \int_1^2 \left[c_v(T)\frac{dT}{T} + R\frac{d\nu}{\nu} \right]$$

$$\Delta s = \int_1^2 c_v(T)\frac{dT}{T} + Rln\frac{\nu_2}{\nu_1}$$

THE ENTROPY CHANGE OF IDEAL GASES

$$ds = \frac{dh}{T} - \nu\frac{dP}{T}$$

Recall Ideal Gas Equation:

$$\nu = \frac{RT}{P}$$

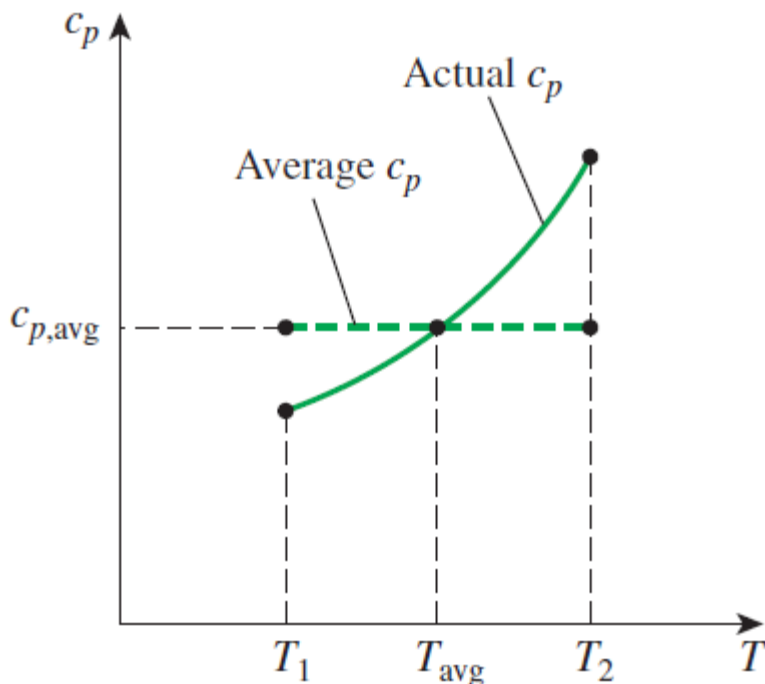$$\Delta s = s_2 - s_1 = \int_1^2 \left[c_p(T)\frac{dT}{T} - R\frac{dP}{P} \right]$$

$$\Delta s = \int_1^2 c_p(T)\frac{dT}{T} - Rln\frac{P_2}{P_1}$$

Constant Specific Heats (Approximate Analysis)

$$s_2 - s_1 = \int_1^2 c_v(T) \frac{dT}{T} + R \ln \frac{v_2}{v_1} \longrightarrow s_2 - s_1 = c_{v,avg} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$

$$s_2 - s_1 = \int_1^2 c_p(T) \frac{dT}{T} - R \ln \frac{P_2}{P_1} \longrightarrow s_2 - s_1 = c_{p,avg} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$(kJ/kg \cdot K)$$

Entropy change of an ideal gas on a unit–mole basis

$$\bar{s}_2 - \bar{s}_1 = \bar{c}_{v,avg} \ln \frac{T_2}{T_1} + R_u \ln \frac{v_2}{v_1} \qquad (kJ/kmol \cdot K)$$

$$\bar{s}_2 - \bar{s}_1 = \bar{c}_{p,avg} \ln \frac{T_2}{T_1} - R_u \ln \frac{P_2}{P_1} \qquad (kJ/kmol \cdot K)$$

FIGURE 7–31

Under the constant-specific-heat assumption, the specific heat is assumed to be constant at some average value.

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Variable Specific Heats (Exact Analysis)

We choose absolute zero as the reference temperature and define a function $s°$ as

$$s° = \int_0^T c_p(T) \frac{dT}{T}$$

$$\int_1^2 c_p(T) \frac{dT}{T} = s_2° - s_1°$$

On a unit–mass basis

$$s_2 - s_1 = s_2° - s_1° - R \ln \frac{P_2}{P_1} \qquad (\text{kJ/kg} \cdot \text{K})$$

On a unit–mole basis

$$\bar{s}_2 - \bar{s}_1 = \bar{s}_2° - \bar{s}_1° - R_u \ln \frac{P_2}{P_1} \qquad (\text{kJ/kmol} \cdot \text{K})$$

T, K	$s°$, kJ/kg·K
⋮	⋮
300	1.70203
310	1.73498
320	1.76690
⋮	⋮

(Table A-17)

FIGURE 7–32

The entropy of an ideal gas depends on both T and P. The function $s°$ represents only the temperature-dependent part of entropy.

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Entropy Change of an Ideal Gas

Air is compressed from an initial state of 100 kPa and 17°C to a final state of 600 kPa and 57°C. Determine the entropy change of air during this compression process (a) by using the property tables and (b) by using an average specific heat.

Example 3

Isentropic Process of Ideal Gases

Constant Specific Heats (Approximate Analysis)

$$\Delta s = 0 = c_{v,avg} ln\frac{T_2}{T_1} + R ln\frac{\nu_2}{\nu_1}$$

$$ln\frac{T_2}{T_1} = -\frac{R}{c_v} ln\frac{\nu_2}{\nu_1}$$

Recall for an ideal gas:

$$R = c_p - c_v \qquad\qquad k = \frac{c_p}{c_v}$$

$$ln\frac{T_2}{T_1} = -\frac{(c_p - c_v)}{c_v} ln\frac{\nu_2}{\nu_1} = -(k-1) ln\frac{\nu_2}{\nu_1}$$

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Isentropic Process of Ideal Gases

Constant Specific Heats (Approximate Analysis)

$$ln\frac{T_2}{T_1} = -(k-1)\,ln\frac{\nu_2}{\nu_1}$$

$$ln\frac{T_2}{T_1} = ln\left(\frac{\nu_2}{\nu_1}\right)^{-(k-1)} = ln\left(\frac{\nu_1}{\nu_2}\right)^{k-1}$$

$$\left(\frac{T_2}{T_1}\right)_{s=const.} = \left(\frac{\nu_1}{\nu_2}\right)^{k-1}$$

Isentropic Process of Ideal Gases

Constant Specific Heats (Approximate Analysis)

$$\Delta s = 0 = c_{p,avg} ln\frac{T_2}{T_1} - R ln\frac{P_2}{P_1}$$

$$ln\frac{T_2}{T_1} = \frac{R}{c_p} ln\frac{P_2}{P_1}$$

Recall for an ideal gas:

$$R = c_p - c_v \qquad\qquad k = \frac{c_p}{c_v}$$

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

Isentropic Process of Ideal Gases

Constant Specific Heats (Approximate Analysis)

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

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

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

Isentropic Process of Ideal Gases

Constant Specific Heats (Approximate Analysis)

$$\left(\frac{T_2}{T_1}\right)_{s=const.} = \left(\frac{P_2}{P_1}\right)^{\left(\frac{k-1}{k}\right)} = \left(\frac{\nu_1}{\nu_2}\right)^{k-1}$$

$$\left(\frac{P_2}{P_1}\right)_{s=const.} = \left(\frac{\nu_1}{\nu_2}\right)^{k}$$

$$T\nu^{k-1} = const.$$

$$TP^{\frac{1-k}{k}} = const.$$

$$P\nu^{k} = const.$$

Isentropic Processes of Ideal Gases

Constant Specific Heats (Approximate Analysis)

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

Setting this eq. equal to zero, we get

$$\ln \frac{T_2}{T_1} = -\frac{R}{c_v} \ln \frac{v_2}{v_1}$$

$$\ln \frac{T_2}{T_1} = \ln \left(\frac{v_1}{v_2} \right)^{R/c_v}$$

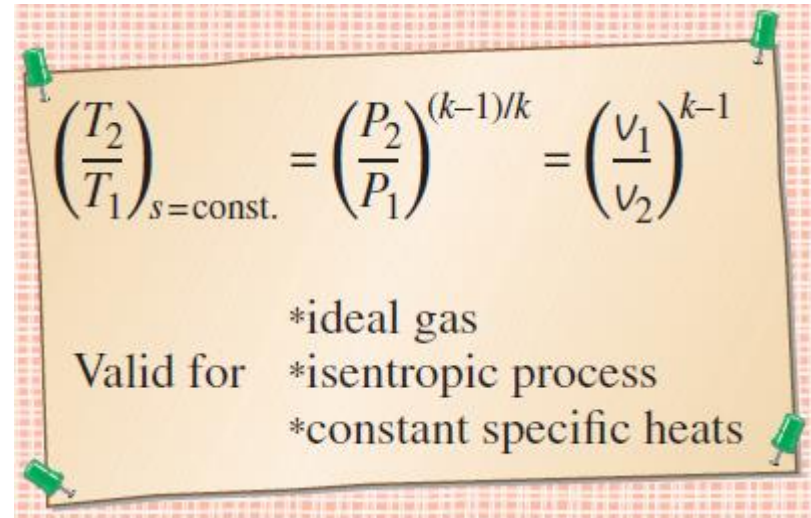$R = c_p - c_v$, $k = c_p/c_v$
and thus $R/c_v = k - 1$

$$\left(\frac{T_2}{T_1} \right)_{s=\text{const.}} = \left(\frac{v_1}{v_2} \right)^{k-1}$$

$$\left(\frac{T_2}{T_1} \right)_{s=\text{const.}} = \left(\frac{P_2}{P_1} \right)^{(k-1)/k}$$

$$\left(\frac{P_2}{P_1} \right)_{s=\text{const.}} = \left(\frac{v_1}{v_2} \right)^{k}$$

$$\left(\frac{T_2}{T_1} \right)_{s=\text{const.}} = \left(\frac{P_2}{P_1} \right)^{(k-1)/k} = \left(\frac{v_1}{v_2} \right)^{k-1}$$

Valid for
*ideal gas
*isentropic process
*constant specific heats

FIGURE 7–35

The isentropic relations of ideal gases are valid for the isentropic processes of ideal gases only.

$$Tv^{k-1} = \text{constant}$$

$$TP^{(1-k)/k} = \text{constant}$$

$$Pv^{k} = \text{constant}$$

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 pressure of the helium at the exit.

Example 4

Isentropic Processes of Ideal Gases

Variable Specific Heats (Exact Analysis)

$$0 = s_2^\circ - s_1^\circ - R \ln \frac{P_2}{P_1} \longrightarrow s_2^\circ = s_1^\circ + R \ln \frac{P_2}{P_1}$$

Relative Pressure and Relative Specific Volume

$$\frac{P_2}{P_1} = \exp \frac{s_2^\circ - s_1^\circ}{R}$$

$\exp(s^\circ/R)$ is the relative pressure P_r.

$$\frac{P_2}{P_1} = \frac{\exp(s_2^\circ /R)}{\exp(s_1^\circ /R)}$$

$$\left(\frac{P_2}{P_1} \right)_{s=\text{const.}} = \frac{P_{r2}}{P_{r1}}$$

$$\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2} \longrightarrow \frac{v_2}{v_1} = \frac{T_2}{T_1} \frac{P_1}{P_2} = \frac{T_2}{T_1} \frac{P_{r1}}{P_{r2}} = \frac{T_2/P_{r2}}{T_1/P_{r1}}$$

$$\left(\frac{v_2}{v_1} \right)_{s=\text{const.}} = \frac{v_{r2}}{v_{r1}}$$
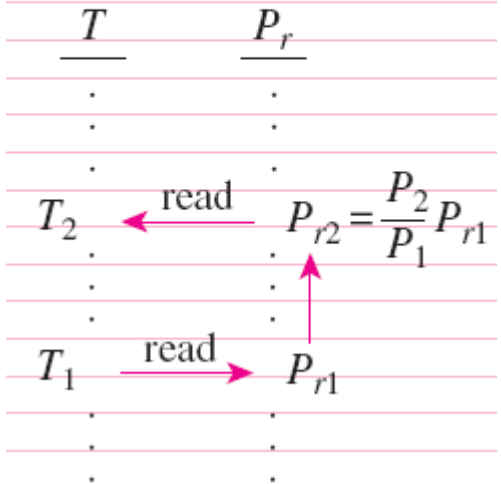
T/P_r is the relative specific volume v_r.

The use of P_r data for calculating the final temperature during an isentropic process.

The use of v_r data for calculating the final temperature during an isentropic process
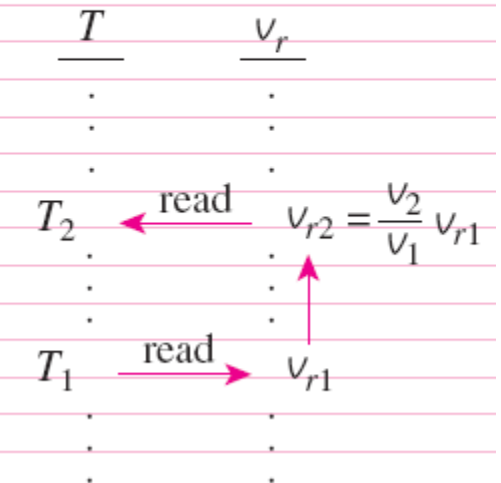
Process: isentropic
Given: P_1, T_1, and P_2
Find: T_2

T	P_r
·	·
·	·
·	·
·	·
$T_2 \xleftarrow{\text{read}}$	$P_{r2} = \frac{P_2}{P_1} P_{r1}$
·	·
·	·
$T_1 \xrightarrow{\text{read}}$	P_{r1}
·	·

Process: isentropic
Given: v_1, T_1, and v_2
Find: T_2

T	v_r
·	·
·	·
·	·
·	·
$T_2 \xleftarrow{\text{read}}$	$v_{r2} = \frac{v_2}{v_1} v_{r1}$
·	·
·	·
$T_1 \xrightarrow{\text{read}}$	v_{r1}
·	·

Practice

Air is compressed in a car engine from 22°C and 95 kPa in a reversible and adiabatic manner. If the compression ratio (v_1/v_2) of the engine is 8, determine the final temperature of the air.

Example 5

Summary

- The *T ds* relations
- Entropy change of liquids and solids
- The entropy change of ideal gases