

Thermodynamics: An Engineering Approach
8th Edition

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McGraw-Hill, 2015

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:

$$h = u + Pv$$

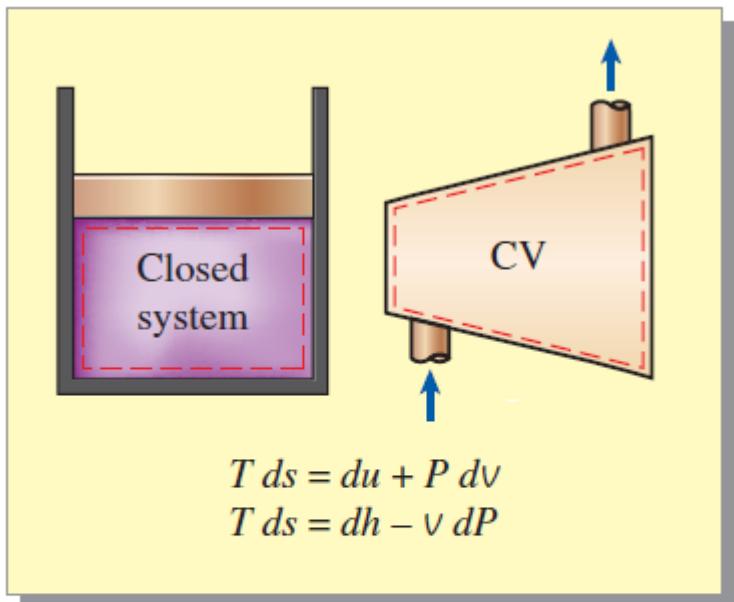
$$dh = du + d(Pv) = du + \nu dP + Pd\nu$$

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

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

$$Tds = dh - \nu dP$$

The T ds Relations



The first Tds relation: (Gibbs Equation)

$$Tds = du + Pd\nu$$

The second Tds relation:

$$Tds = dh - \nu dP$$

We can solve for ds in both equations:

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

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

FIGURE 7–27

The Tds relations are valid for both reversible and irreversible processes and for both closed and open systems.

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 isothermal.

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

Solution

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?

Solution

THE ENTROPY CHANGE OF IDEAL GASES

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

Recall Ideal Gas Equation:

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

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

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

THE ENTROPY CHANGE OF IDEAL GASES

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

Recall Ideal Gas Equation:

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

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

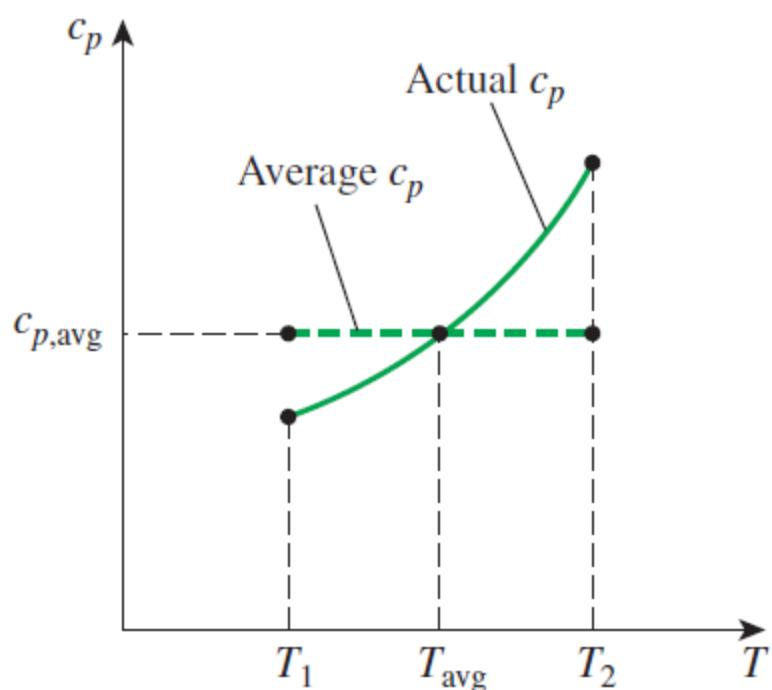
$$\Delta s = \int_1^2 c_p(T) \frac{dT}{T} - R \ln \frac{P_2}{P_1}$$

Constant Specific Heats (Approximate Analysis)

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

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

(kJ/kg · K)



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

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

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

FIGURE 7–31

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

Variable Specific Heats (Exact Analysis)

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

$$s^\circ = \int_0^T c_p(T) \frac{dT}{T}$$

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

On a unit-mass basis

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

On a unit-mole basis

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

<u>T, K</u>	<u>s°, kJ/kg·K</u>
.	.
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.

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.

Solution

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:

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

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

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:

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

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

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 $R/c_v = k - 1$

$$\left(\frac{T_2}{T_1} \right)_{s=\text{const.}} = \left(\frac{V_1}{V_2} \right)^{k-1}$$

$$\left(\frac{T_2}{T_1} \right)_{s=\text{const.}} = \left(\frac{P_2}{P_1} \right)^{(k-1)/k} \left(\frac{P_2}{P_1} \right)_{s=\text{const.}} = \left(\frac{V_1}{V_2} \right)^k \quad TP^{(1-k)/k} = \text{constant}$$
$$P V^k = \text{constant}$$

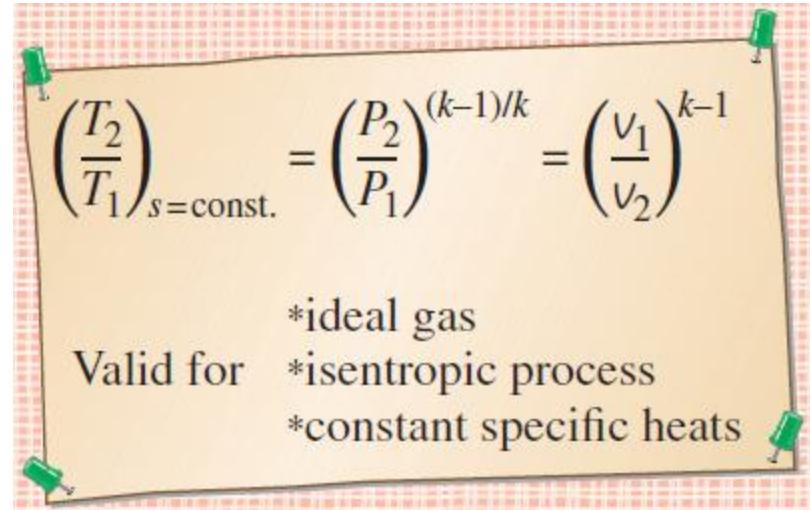


FIGURE 7–35

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

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

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.

Solution

Isentropic Processes of Ideal Gases

Variable Specific Heats (Exact Analysis)

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

Relative Pressure and Relative Specific Volume

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

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

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

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

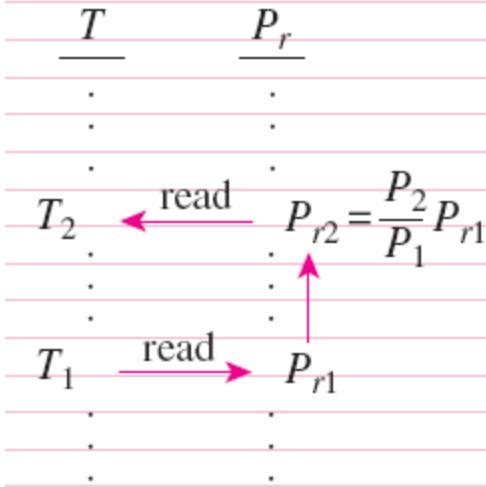
$$\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2} \rightarrow \frac{v_2}{v_1} = \frac{T_2}{T_1} \frac{P_1}{P_2} = \frac{T_2}{T_1} \frac{P_{r1}}{P_{r2}} = \frac{T_2/P_{r2}}{T_1/P_{r1}}$$

$$\left(\frac{v_2}{v_1} \right)_{s=\text{const.}} = \frac{v_{r2}}{v_{r1}}$$

T/P_r is the relative specific volume v_r

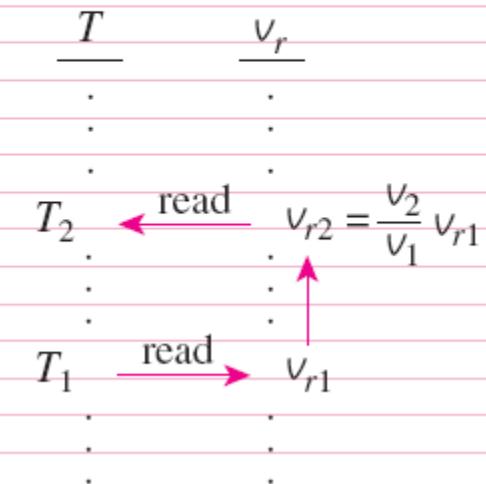
The use of P_r data for calculating the final temperature during an isentropic process.

Process: isentropic
Given: P_1 , T_1 , and P_2
Find: T_2



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

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



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.

Solution

Summary

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