Thermodynamics: An Engineering Approach
8th Edition
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# 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

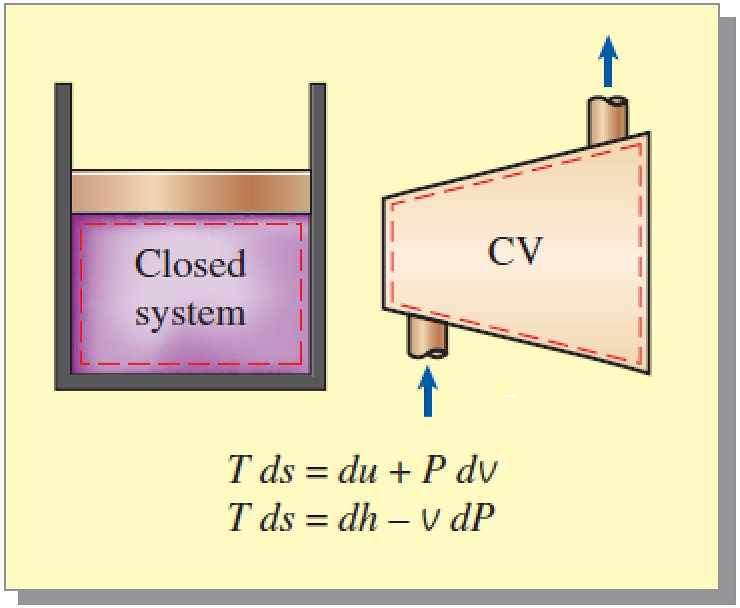



**FIGURE 7–27**
The $T\,ds$ relations are valid for both reversible and irreversible processes and for both closed and open systems.

The first *Tds* relation: (Gibbs Equation)

$$Tds = du + Pd\nu$$

The second *Tds* relation:

$$Tds = dh - \nu dP$$

We can solve for *ds* in both equations:

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

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

# ENTROPY CHANGE OF LIQUIDS AND SOLIDS

Recall liquids and solids are incompressible substances.

$$d\nu \cong 0$$

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

Recall specific heat equations:

$$du = cdT$$

For liquids and solids $c_p = c_v = c$

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

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

# 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<br>T, K | Pressure<br>P, MPa | Density<br>$\rho$, kg/m$^3$ | Enthalpy<br>h, kJ/kg | Entropy<br>s, kJ/kg K | Specific Heat<br>$c_p$, 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 $m^3$/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:

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

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

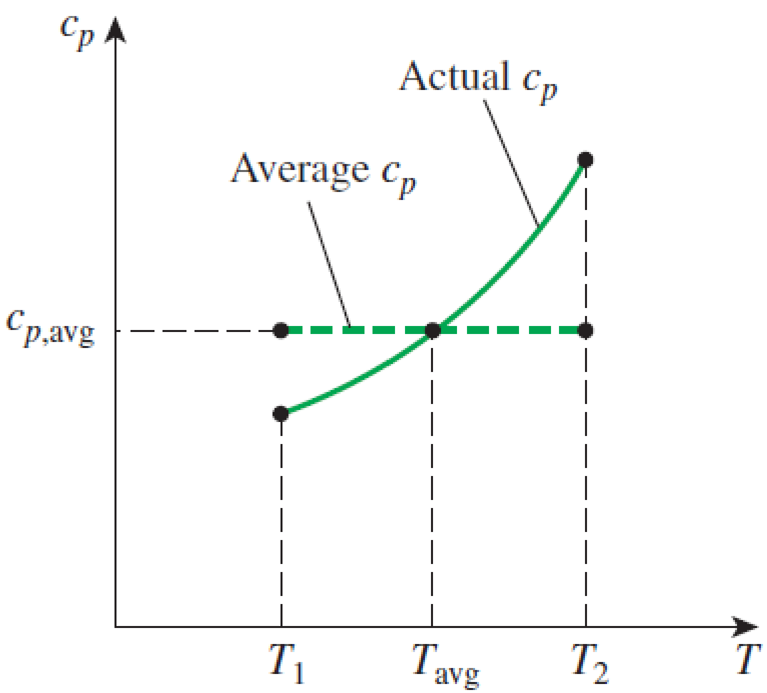
$$\Delta s = \int_1^2 c_p(T) \frac{dT}{T} - R ln \frac{P_2}{P_1}$$

# Constant Specific Heats (Approximate Analysis)

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

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

$$(\text{kJ/kg}\cdot\text{K})$$




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

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

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

**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

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

On a unit–mole basis

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

| $T$, K | $s^\circ$, 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 $s^\circ$ 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.

**Example 3**

# Isentropic Process of Ideal Gases

**Constant Specific Heats (Approximate Analysis)**

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

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

Recall for an ideal gas:

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

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

# Isentropic Process of Ideal Gases

**Constant Specific Heats (Approximate Analysis)**

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

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

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

# Isentropic Process of Ideal Gases

**Constant Specific Heats (Approximate Analysis)**

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

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

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 $R/c_v = k - 1$

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

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

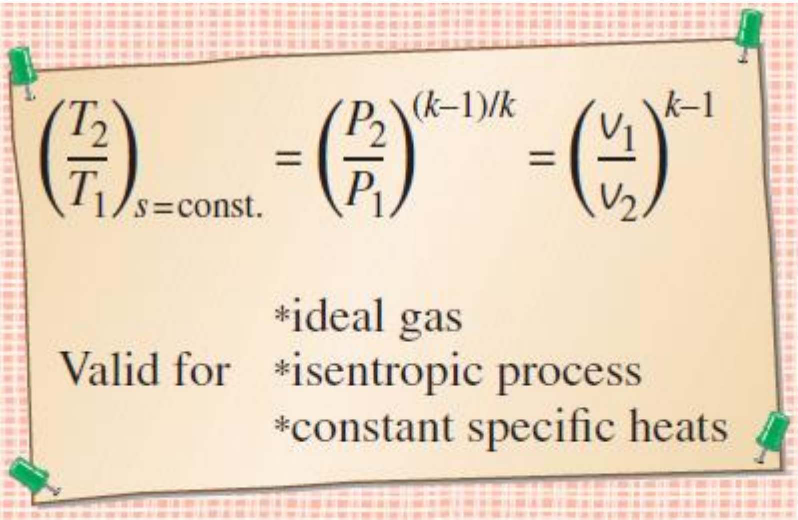



**FIGURE 7–35**
The isentropic relations of ideal gases are valid for the isentropic processes of ideal gases only.

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

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

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

# 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

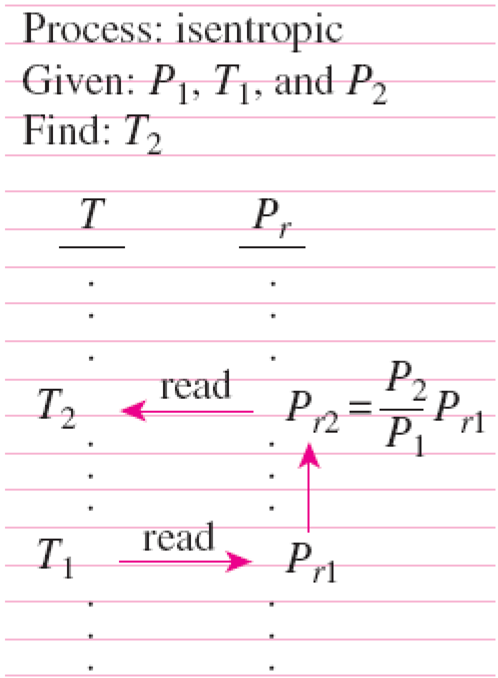
$$\frac{P_2}{P_1} = \exp\frac{s_2^\circ - s_1^\circ}{R}$$

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

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

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

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

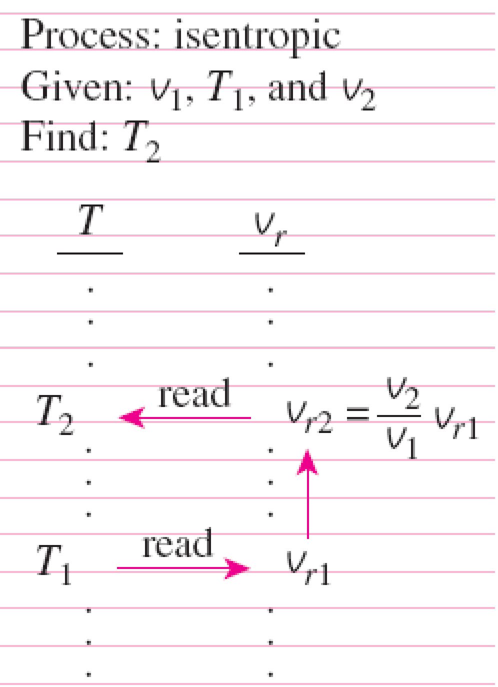



$$\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2} \rightarrow \frac{v_2}{v_1} = \frac{T_2}{T_1}\frac{P_1}{P_2} = \frac{T_2}{T_1}\frac{P_{r1}}{P_{r2}} = \frac{T_2/P_{r2}}{T_1/P_{r1}}$$

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

$T/P_r$ is the relative specific volume $v_r$.

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



# Practice

Air is compressed in a car engine from 22$^{o}$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