Chapter Six

Consequences of the second law of thermodynamics and entropy

6.1 Introduction

- For overcoming the limitations of first law, the second law of thermodynamics had been stated.
- Now we need some mathematical parameter for being used as decision maker in respect of feasibility of process, irreversibility, nature of process etc.
- Here in this chapter a mathematical function called ‘entropy’ has been explained.
- Entropy is the outcome of second law and is a thermodynamic property.
- Entropy is defined in the form of calculus operation, hence no exact physical description of it can be given. However, it has enormous significance in thermodynamic process analysis.

6.2 CLAUSIUS INEQUALITY

- The second law of thermodynamics often leads to expressions that involve inequalities. An irreversible (i.e., actual) heat engine, for example, is less efficient than a reversible one operating between the same two thermal energy reservoirs.
- Likewise, an irreversible refrigerator or a heat pump has a lower coefficient of performance (COP) than a reversible one operating between the same temperature limits.
- Another important inequality that has major consequences in thermodynamics is the **Clausius inequality.** It was first stated by the German physicist R. J. E. Clausius (1822–1888), one of the founders of thermodynamics, and is expressed as

$$\oint \frac{\delta Q}{T} \leq 0$$

Cont..

- This inequality is valid for all thermodynamic cycles, reversible or irreversible.
- In the reversed cycle case, all the quantities have the same magnitude but the opposite sign.

$$\oint \left(\frac{\delta Q}{T}\right)_{\text{int rev}} = 0$$

- we conclude that the equality in the Clausius inequality holds for totally or just internally reversible cycles and the inequality for the irreversible ones.

here,

$$\oint \left(\frac{dQ}{T}\right) = 0 \text{ for reversible cycle}$$

$$\oint \left(\frac{dQ}{T}\right) < 0, \text{ for irreversible cycle}$$

$$\oint \left(\frac{dQ}{T}\right) > 0, \text{ for impossible cycle}$$

6.3 Defining Entropy Change

- A quantity is a property if, and only if, its change in value between two states is independent of the process
- Using this concept and Clausius inequality equation we can define a new property let us see
- Two cycles executed by a closed system are represented in Figure below. One cycle consists of an internally reversible process A from state 1 to state 2, followed by internally reversible process C from state 2 to state 1.
- The other cycle consists of an internally reversible process B from state 1 to state 2, followed by the same process C from state 2 to state 1 as in the first cycle. For the first cycle, Clausius inequality takes the form

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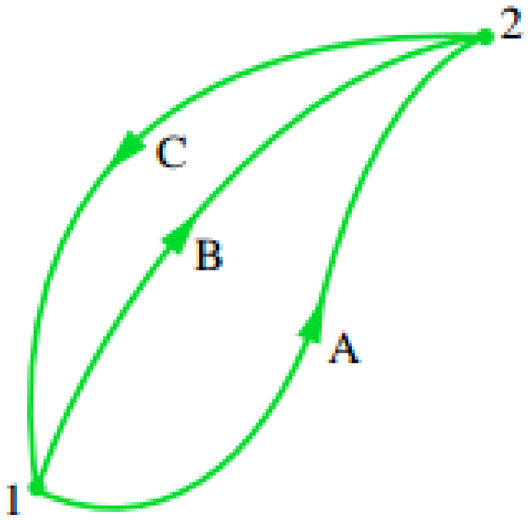

Figure 6.3 Two internally reversible cycles

$$\left(\int_1^2 \frac{\delta Q}{T}\right)_A + \left(\int_2^1 \frac{\delta Q}{T}\right)_C = 0$$

and for the second cycle

$$\left(\int_1^2 \frac{\delta Q}{T}\right)_B + \left(\int_2^1 \frac{\delta Q}{T}\right)_C = 0$$

Cont..

- Then subtract the second equation from the first one and we will have

$$\left(\int_1^2 \frac{\delta Q}{T}\right)_A = \left(\int_1^2 \frac{\delta Q}{T}\right)_B$$

- This shows that the integral of δQ/T is the same for both processes.
- Since A and B are arbitrary, it follows that the integral of δQ/T has the same value for *any* internally reversible process between the two states.
- In other words, the value of the integral depends on the end states only. It can be concluded, therefore, that the integral represents the change in some property of the system. Selecting the symbol *S* to denote this property, which is called *entropy*, its change is given by

$$S_2 - S_1 = \left(\int_1^2 \frac{\delta Q}{T}\right)_{\substack{\text{int}\\ \text{rev}}}$$

Cont..

- This is the ***definition of entropy change.*** On a differential basis, the defining equation for entropy change takes the form

$$dS = \left(\frac{\delta Q}{T}\right)_{\substack{\text{int}\\ \text{rev}}}$$

- Entropy is an extensive property. The ***SI unit for entropy*** is J/K. However, in this book it is convenient to work in terms of kJ/K. Units in SI for *specific* entropy are kJ/kg K.
- Since entropy is a property, the change in entropy of a system in going from one state to another is the same for *all* processes, both internally reversible and irreversible, between these two states.
- Thus, the above equation allows the determination of the change in entropy, and once it has been evaluated, this is the magnitude of the entropy change for all processes of the system between the two states.

Cont..

A Special Case: Internally Reversible Isothermal Heat Transfer Processes

isothermal heat transfer processes are internally reversible. Therefore, the entropy change of a system during an internally reversible isothermal heat transfer process can be determined by performing the integration in the above equation:

$$\Delta S = \int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{int rev}} = \int_1^2 \left(\frac{\delta Q}{T_0}\right)_{\text{int rev}} = \frac{1}{T_0}\int_1^2 (\delta Q)_{\text{int rev}}$$

which reduces to

$$\Delta S = \frac{Q}{T_0} \qquad \text{(kJ/K)}$$

- Where: T_o is the constant temperature of the system and Q is the heat transfer for the internally reversible process.

Cont..

- The above Equation is particularly useful for determining the entropy changes of thermal energy reservoirs that can absorb or supply heat indefinitely at a constant temperature.
- Notice that the entropy change of a system during an internally reversible isothermal process can be positive or negative, depending on the direction of heat transfer.
- Heat transfer to a system increases the entropy of a system, whereas heat transfer from a system decreases it. In fact, losing heat is the only way the entropy of a system can be decreased.

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Example

1. A piston–cylinder device contains a liquid–vapor mixture of water at 300 K. During a constant-pressure process, 750 kJ of heat is transferred to the water. As a result, part of the liquid in the cylinder vaporizes. Determine the entropy change of the water during this process.

6.4 Retrieving Entropy Data

- The entropy values in the property tables are given relative to an arbitrary reference state.
- In steam tables the entropy of saturated liquid s_f at 0.01°C is assigned the value of zero.
- For refrigerant-134a, the zero value is assigned to saturated liquid at -40°C.
- The entropy values become negative at temperatures below the reference value.
- The value of entropy at a specified state is determined just like any other property.
- In the compressed liquid and superheated vapor regions, it can be obtained directly from the tables at the specified state.
- In the saturated mixture region, it is determined from

$$s = s_f + x s_{fg} \qquad (\mathrm{kJ/kg \cdot K})$$

Cont..

- In the absence of compressed liquid data, the entropy of the compressed liquid can be approximated by the entropy of the saturated liquid at the given temperature

$$s_{@\,T,P} \cong s_{f\,@\,T} \qquad (\mathrm{kJ/kg\cdot K})$$

- The entropy change of a specified mass *m* (a closed system) during a process is simply

$$\Delta S = m\Delta s = m(s_2 - s_1) \qquad (\mathrm{kJ/K})$$

- which is the difference between the entropy values at the final and initial states.

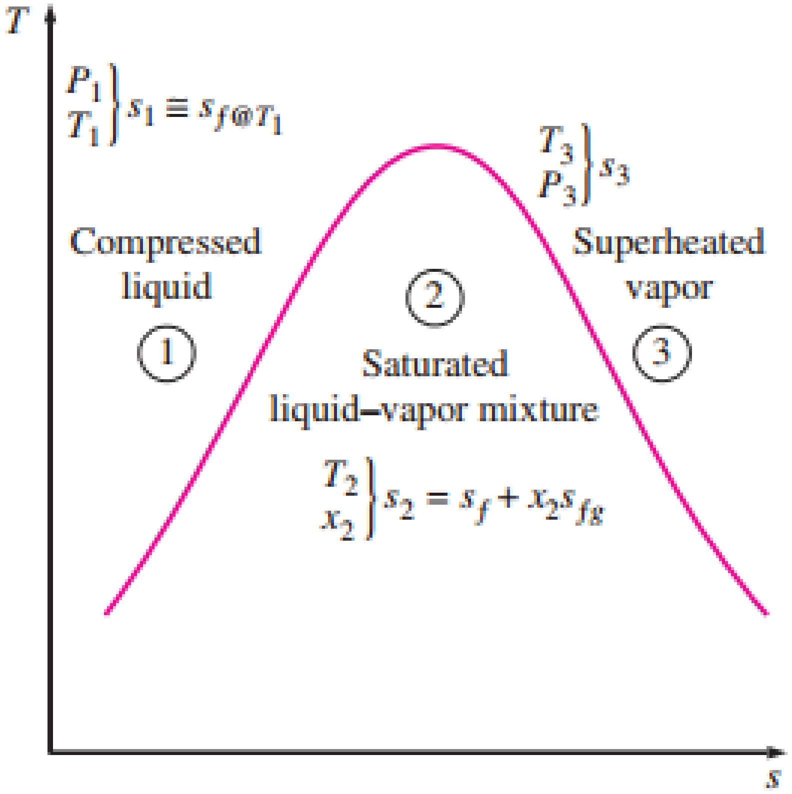

Fig: The entropy of a pure substance is determined from the tables (like other properties).

Using Graphical Entropy Data

- When studying the second-law aspects of processes, entropy is commonly used as a coordinate on diagrams such as the *T-s* and *h-s* diagrams.
- The general characteristics of the *T-s* diagram of pure substances are shown in Fig. below using data for water.
- Notice from this diagram that the constant volume lines are steeper than the constant-pressure lines and the constant pressure lines are parallel to the constant-temperature lines in the saturated liquid–vapor mixture region.
- Also, the constant-pressure lines almost coincide with the saturated liquid line in the compressed liquid region.

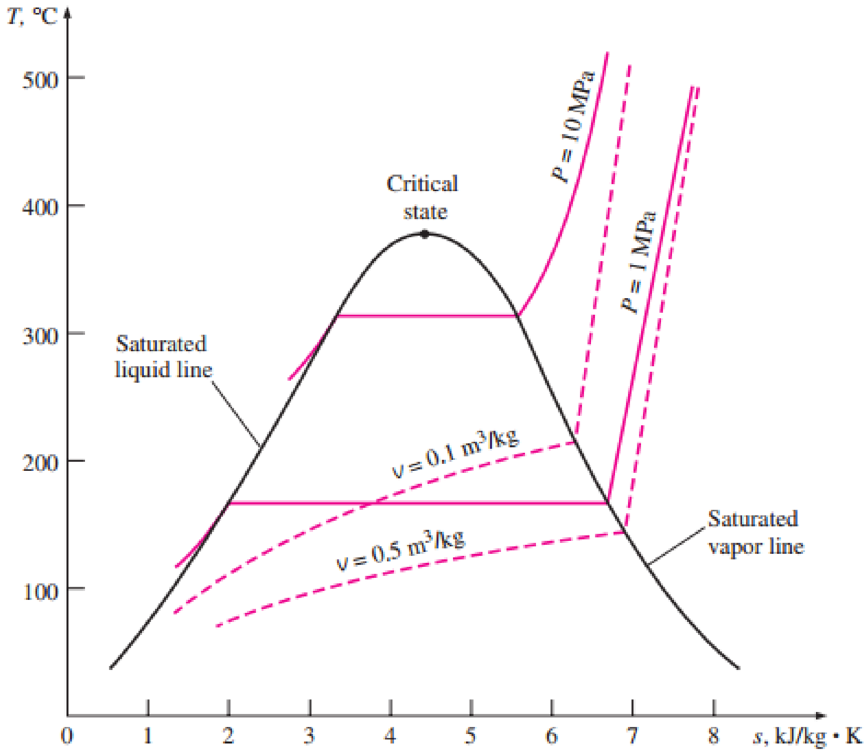

Fig: Schematic of the *T-s* diagram for water.

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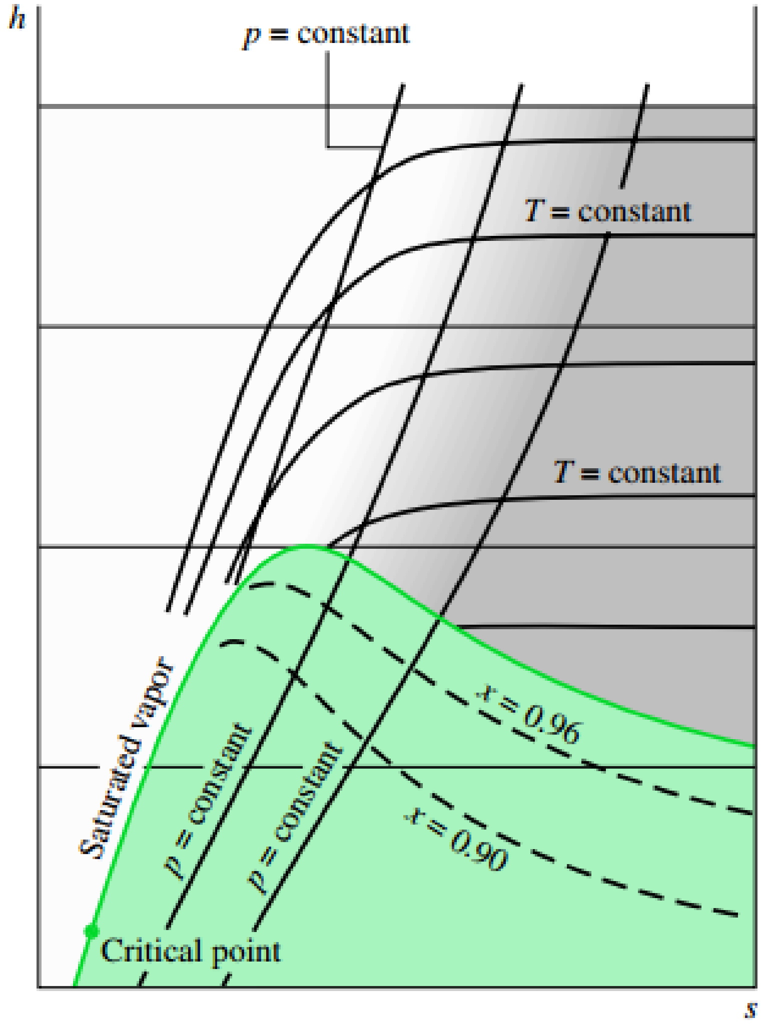
Enthalpy–Entropy Diagram

- The essential features of an enthalpy–entropy diagram, commonly known as a ***Mollier diagram,*** are shown in Fig. below.
- The general characteristics of the *h*-*s* diagram of pure substances are shown in Fig. below using data for water.
- Lines of constant quality are shown in the two phase liquid–vapor region . The figure is intended for evaluating properties at superheated vapor states and for two-phase liquid– vapor mixtures.
- Liquid data are seldom shown. In the superheated vapor region, constant temperature lines become nearly horizontal as pressure is reduced.



▲ **Figure 6.4** Enthalpy–entropy diagram.

Example

1. A rigid tank contains 5 kg of refrigerant-134a initially at 20°C and 140 kPa. The refrigerant is now cooled while being stirred until its pressure drops to 100 kPa. Determine the entropy change of the refrigerant during this process.

Using The *T dS* Equations

- The *T dS* equations are developed by considering a pure, simple compressible system undergoing an internally reversible process. In the absence of overall system motion and the effects of gravity, an energy balance in differential form is

$$(\delta Q)_{\substack{\text{int}\\\text{rev}}} = dU + (\delta W)_{\substack{\text{int}\\\text{rev}}}$$

- By definition of simple compressible system the work is

$$(\delta W)_{\substack{\text{int}\\\text{rev}}} = p\,dV$$

- the heat transfer is $(\delta Q)_{\substack{\text{int}\\\text{rev}}} = T\,dS$

- Substitute this two equation from Tds then

$$T\,dS = dU + p\,dV$$

Cont..

- The *second T dS* equation is obtained from using

$$H = U + pV.$$

- Forming the differential

$$dH = dU + d(pV) = dU + p\,dV + V\,dp$$

- Rearrange this equation

$$dU + p\,dV = dH - V\,dp$$

Therefore

$$T\,dS = dH - V\,dp$$

- The *T dS* equations can be written on a unit mass basis as

$$T\,ds = du + p\,dv$$

$$T\,ds = dh - v\,dp$$

Cont..

- Although the *T dS* equations are derived by considering an internally reversible process, an entropy change obtained by integrating these equations is the change for *any* process, reversible or irreversible, between two equilibrium states of a system.
- Because entropy is a property, the change in entropy between two states is independent of the details of the process linking the states.
- To show the use of the *T dS* equations, consider a change in phase from saturated liquid to saturated vapor at constant temperature and pressure. Since pressure is constant, $Tds = dh + vdp$ reduces to give

$$ds = \frac{dh}{T}$$

- Then, because temperature is also constant during the phase change

$$s_g - s_f = \frac{h_g - h_f}{T}$$

Entropy Change of an Ideal Gas

- In this section the *T dS* equations are used to evaluate the entropy change between two states of an ideal gas. It is convenient to begin with

$$T\,ds = du + p\,dv$$

$$T\,ds = dh - v\,dp$$

$$ds = \frac{du}{T} + \frac{p}{T}dv$$

$$ds = \frac{dh}{T} - \frac{v}{T}dp$$

For an ideal gas, $du = c_v(T)dT$, $dh = c_p(T)dT$, and $pv = RT$. With these relations, the above equation become, respectively

$$ds = c_v(T)\frac{dT}{T} + R\frac{dv}{v} \qquad \text{and} \qquad ds = c_p(T)\frac{dT}{T} - R\frac{dp}{p}$$

Cont..

- Since *R* is a constant, the last terms of the above Equation can be integrated directly.
- However, because *cv* and *cp* are functions of temperature for ideal gases, it is necessary to have information about the functional relationships before the integration of the first term in these equations can be performed.
- Since the two specific heats are related by

$$c_p(T) = c_v(T) + R$$

where *R* is the gas constant, knowledge of either specific heat function be enough. On integration

$$s(T_2, v_2) - s(T_1, v_1) = \int_{T_1}^{T_2} c_v(T) \frac{dT}{T} + R \ln \frac{v_2}{v_1}$$

$$s(T_2, p_2) - s(T_1, p_1) = \int_{T_1}^{T_2} c_p(T) \frac{dT}{T} - R \ln \frac{p_2}{p_1}$$

USING IDEAL GAS TABLES. As for internal energy and enthalpy changes, the evaluation of entropy changes for ideal gases can be reduced to a convenient tabular approach. To introduce this, we begin by selecting a reference state and reference value: The value of the specific entropy is set to zero at the state where the temperature is 0 K and the pressure is 1 atmosphere. Then, using Eq. 6.19, the specific entropy at a state where the temperature is T and the pressure is 1 atm is determined relative to this reference state and reference value as

$$s^\circ(T) = \int_0^T \frac{c_p(T)}{T}\, dT \tag{6.20}$$

The symbol $s^\circ(T)$ denotes the specific entropy at temperature T and *a pressure of 1 atm*. Because s° depends only on temperature, it can be tabulated versus temperature, like h and u. For air as an ideal gas, s° with units of kJ/kg · K is given in Tables A-22. Values of $\bar{s}^\circ$ for several other common gases are given in Tables A-23 with units of kJ/kmol · K. Since the integral of Eq. 6.19 can be expressed in terms of s°

$$\begin{aligned}\int_{T_1}^{T_2} c_p \frac{dT}{T} &= \int_0^{T_2} c_p \frac{dT}{T} - \int_0^{T_1} c_p \frac{dT}{T} \\ &= s^\circ(T_2) - s^\circ(T_1)\end{aligned}$$

Cont..

- it follows that Eq. 6.19 can be written as

$$s(T_2, p_2) - s(T_1, p_1) = s^\circ(T_2) - s^\circ(T_1) - R \ln \frac{p_2}{p_1}$$

Example

1. Evaluate the change in specific entropy, in kJ/kg K, of air modeled as an ideal gas from a state where $T_1 = 300\ K$ and $P_1 = 1 bar$ to a state where $T_2 = 1000\ K$ and $P_2 = 3\ bar$

Cont..

ASSUMING CONSTANT SPECIFIC HEATS

- When the specific heats *cv* and *cp* are taken as constants, equation of change in enthalpy reduce to

$$s(T_2, v_2) - s(T_1, v_1) = c_v \ln\frac{T_2}{T_1} + R \ln\frac{v_2}{v_1}$$

$$s(T_2, p_2) - s(T_1, p_1) = c_p \ln\frac{T_2}{T_1} - R \ln\frac{p_2}{p_1}$$

example

1. determine the change in specific entropy, in of air as an ideal gas undergoing a process from $T1 = 300$ K, $p1 = 1$ bar to $T2 = 400$ K, $p2 = 5$ bar. Because of the relatively small temperature range, we assume a constant value of *cp* evaluated at 350 K. $cp = 1.008$ from Table A-20

Entropy Change of An Incompressible Substance

the specific volume (density) is constant and the specific heat depends solely on temperature, *cv* = *c*(*T*). Accordingly, the differential change in specific internal energy is *du* = *c*(*T*) *dT*

$$ds = \frac{c(T)\,dT}{T} + \cancel{\frac{p\,dv}{T}}^{\,0} = \frac{c(T)\,dT}{T}$$

On integration, the change in specific entropy is

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c(T)}{T}\,dT \qquad \text{(incompressible)}$$

When the specific heat is assumed constant, this becomes

$$s_2 - s_1 = c \ln \frac{T_2}{T_1} \qquad \text{(incompressible, constant } c\text{)}$$

These equation are applicable to liquids and solids modeled as incompressible.

ISENTROPIC PROCESSES

- The entropy of a fixed mass can be changed by (1) heat transfer and (2) irreversibilities. Then it follows that the entropy of a fixed mass does not change during a process that is *internally reversible* and *adiabatic*. A process during which the entropy remains constant is called an **isentropic process.** It is characterized by

Isentropic process: $\Delta s = 0$ or $s_2 = s_1$ (kJ/kg · K)

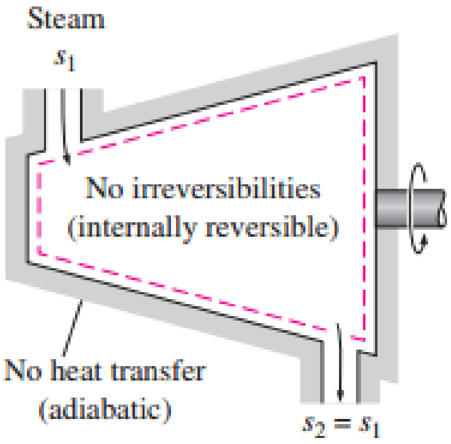


Fig: During an internally reversible, adiabatic (isentropic) process, the entropy remains constant.

Isentropic Processes of Ideal Gases

Constant Specific Heats (Approximate Analysis)

When the constant-specific-heat assumption is valid, the isentropic relations for ideal gases are obtained by setting the change in enthalpy equal to zero.

$$s_2 - s_1 = c_{v,\text{avg}} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \qquad (\text{kJ/kg} \cdot \text{K})$$

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

which can be rearranged as

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

or

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

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

The above equation is the *first isentropic relation* for ideal gases under the constant-specific-heat assumption.

Cont..

- The *second isentropic relation* is obtained in a similar manner from:

$$s_2 - s_1 = c_{p,\text{avg}} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \qquad (\text{kJ/kg} \cdot \text{K})$$

- with the following result:

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

- The *third isentropic relation* is obtained by substituting the second isentropic relation into the first one and simplifying:

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

- The above Equations can also be expressed in a compact form as

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

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

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

- The specific heat ratio *k*, in general, varies with temperature, and thus an average *k* value for the given temperature range should be used.

Cont..

Variable Specific Heats (Exact Analysis)

When the constant-specific-heat assumption is not appropriate, the isentropic relations developed previously yields results that are not quite accurate. For such cases, we should use an isentropic relation obtained from

$$s(T_2, p_2) - s(T_1, p_1) = s^\circ(T_2) - s^\circ(T_1) - R \ln \frac{p_2}{p_1}$$

that accounts for the variation of specific heats with temperature. Setting this equation equal to zero gives

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

or

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

where s_2° is the s° value at the end of the isentropic process.

Cont..

Relative Pressure and Relative Specific Volume

the above isentropic Equations provides an accurate way of evaluating property changes of ideal gases during isentropic processes since it accounts for the variation of specific heats with temperature. However, it involves tedious iterations when the volume ratio is given instead of the pressure ratio.

The definition of the first is based on

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

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

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

Cont..

The quantity $\exp(s°/R)$ is defined as the **relative pressure** P_r. With this definition, the last relation becomes

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

- Note that the relative pressure *Pr* is a *dimensionless* quantity that is a function of temperature only since *s*° depends on temperature alone. Therefore, values of *P r* can be tabulated against temperature. This is done for air in Table A–21.

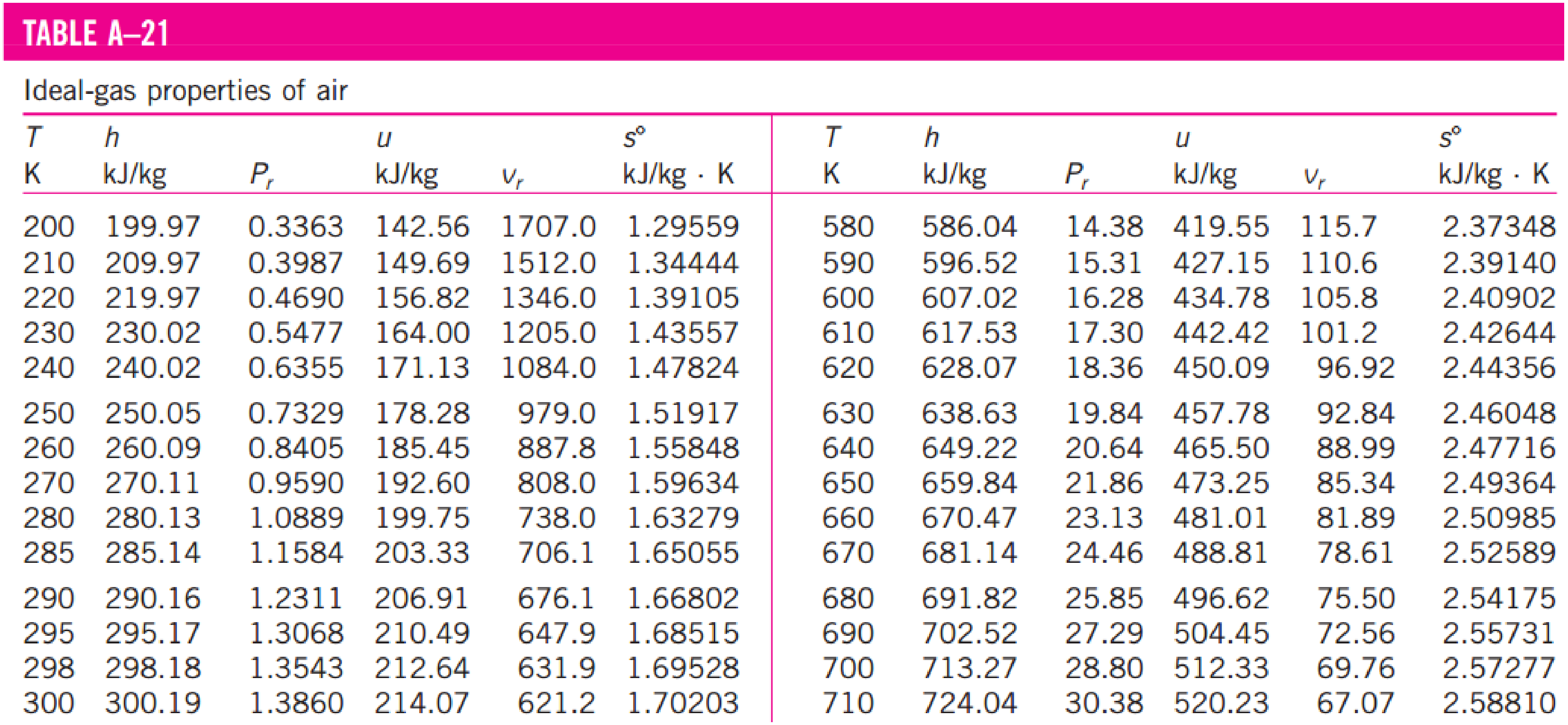


TABLE A–21

Ideal-gas properties of air

T K	h kJ/kg	P_r	u kJ/kg	v_r	$s°$ kJ/kg · K	T K	h kJ/kg	P_r	u kJ/kg	v_r	$s°$ kJ/kg · K
200	199.97	0.3363	142.56	1707.0	1.29559	580	586.04	14.38	419.55	115.7	2.37348
210	209.97	0.3987	149.69	1512.0	1.34444	590	596.52	15.31	427.15	110.6	2.39140
220	219.97	0.4690	156.82	1346.0	1.39105	600	607.02	16.28	434.78	105.8	2.40902
230	230.02	0.5477	164.00	1205.0	1.43557	610	617.53	17.30	442.42	101.2	2.42644
240	240.02	0.6355	171.13	1084.0	1.47824	620	628.07	18.36	450.09	96.92	2.44356
250	250.05	0.7329	178.28	979.0	1.51917	630	638.63	19.84	457.78	92.84	2.46048
260	260.09	0.8405	185.45	887.8	1.55848	640	649.22	20.64	465.50	88.99	2.47716
270	270.11	0.9590	192.60	808.0	1.59634	650	659.84	21.86	473.25	85.34	2.49364
280	280.13	1.0889	199.75	738.0	1.63279	660	670.47	23.13	481.01	81.89	2.50985
285	285.14	1.1584	203.33	706.1	1.65055	670	681.14	24.46	488.81	78.61	2.52589
290	290.16	1.2311	206.91	676.1	1.66802	680	691.82	25.85	496.62	75.50	2.54175
295	295.17	1.3068	210.49	647.9	1.68515	690	702.52	27.29	504.45	72.56	2.55731
298	298.18	1.3543	212.64	631.9	1.69528	700	713.27	28.80	512.33	69.76	2.57277
300	300.19	1.3860	214.07	621.2	1.70203	710	724.04	30.38	520.23	67.07	2.58810

Cont..

- Sometimes specific volume ratios are given instead of pressure ratios. This is particularly the case when automotive engines are analyzed. In such cases, one needs to work with volume ratios. Therefore, we define another quantity related to specific volume ratios for isentropic processes.
- This is done by utilizing the ideal-gas relation and the following equation

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

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

- The quantity *T*/*Pr* is a function of temperature only and is defined as **relative specific volume** *vr*. Thus

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

- This equations are strictly valid for isentropic processes of ideal gases only. They account for the variation of specific heats with temperature and therefore give more accurate results than constant specific heat.

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Example

Air is compressed in a car engine from 22°C and 95 kPa in a reversible and adiabatic manner. If the compression ratio $V1/V2$ of this engine is 8, determine the final temperature of the air.