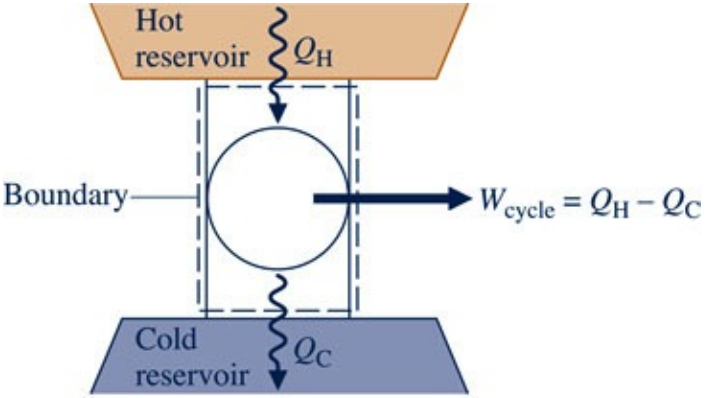
Second Law of Thermodynamics
Alternative Statements

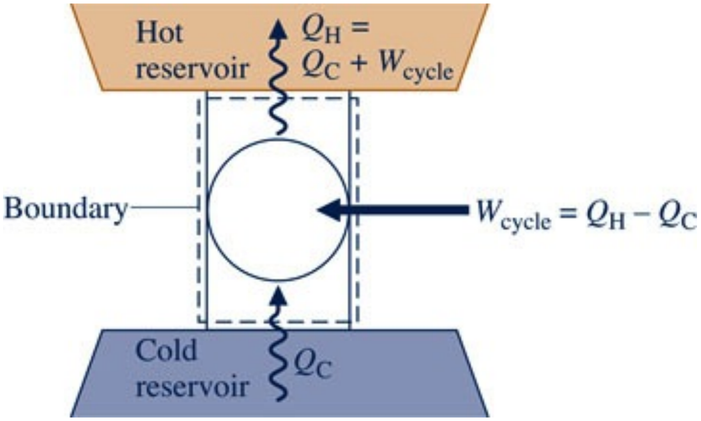
There is no simple statement that captures all aspects of the second law. Several alternative formulations of the second law are found in the technical literature. Three prominent ones are:

- ►Clausius Statement
- ►Kelvin-Planck Statement
- ►Entropy Statement

Kelvin Temperature Scale

Consider systems undergoing a power cycle and a refrigeration or heat pump cycle, each while exchanging energy by heat transfer with hot and cold reservoirs:



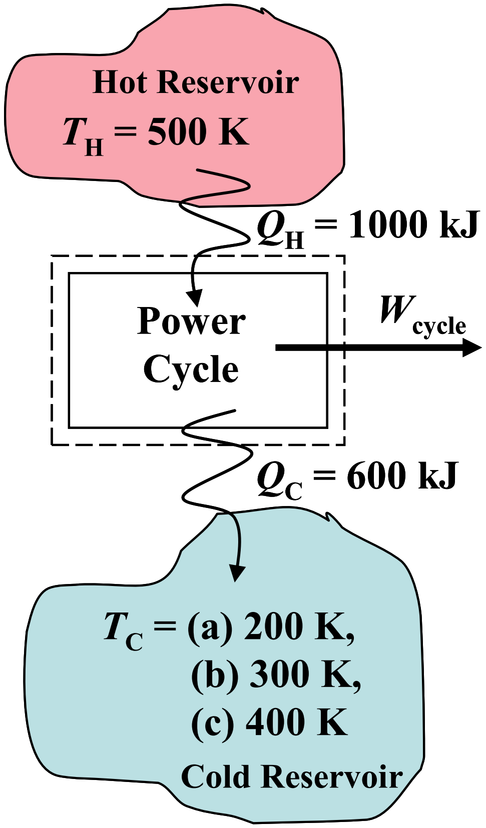


The Kelvin temperature is defined so that

$$\left(\frac{Q_C}{Q_H}\right)_{\substack{\text{rev}\\ \text{cycle}}} = \frac{T_C}{T_H} \qquad \textbf{(Eq. 5.7)}$$

Example: Power Cycle Analysis

A system undergoes a power cycle while receiving 1000 kJ by heat transfer from a thermal reservoir at a temperature of 500 K and discharging 600 kJ by heat transfer to a thermal reservoir at (a) 200 K, (b) 300 K, (c) 400 K. For each case, **determine** whether the cycle operates ***irreversibly***, operates ***reversibly***, or is ***impossible***.



Solution: To determine the nature of the cycle, **compare** actual cycle performance (η) to maximum theoretical cycle performance (η_{max}) calculated from Eq. 5.9

Example: Power Cycle Analysis

Actual Performance: Calculate η using the heat transfers:

$$\eta = 1 - \frac{Q_\mathrm{C}}{Q_\mathrm{H}} = 1 - \frac{600\ \mathrm{kJ}}{1000\ \mathrm{kJ}} = 0.4$$

Maximum Theoretical Performance: Calculate η_max from Eq. 5.9 and compare to η:

		η	η_max	
(a)	$\eta_\mathrm{max} = 1 - \frac{T_\mathrm{C}}{T_\mathrm{H}} = 1 - \frac{200\ \mathrm{K}}{500\ \mathrm{K}} = 0.6$	**0.4**	$<$ **0.6**	→ **Irreversibly**
(b)	$\eta_\mathrm{max} = 1 - \frac{T_\mathrm{C}}{T_\mathrm{H}} = 1 - \frac{300\ \mathrm{K}}{500\ \mathrm{K}} = 0.4$	**0.4**	$=$ **0.4**	→ **Reversibly**
(c)	$\eta_\mathrm{max} = 1 - \frac{T_\mathrm{C}}{T_\mathrm{H}} = 1 - \frac{400\ \mathrm{K}}{500\ \mathrm{K}} = 0.2$	**0.4**	$>$ **0.2**	→ **Impossible**

Clausius Inequality

- ►The Clausius inequality considered next provides the basis for developing the entropy concept in Chapter 6.
- ►The Clausius inequality is applicable to any cycle without regard for the body, or bodies, from which the system undergoing a cycle receives energy by heat transfer or to which the system rejects energy by heat transfer. Such bodies need not be thermal reservoirs.

Clausius Inequality

- ►The Clausius inequality is developed from the Kelvin-Planck statement of the second law and can be expressed as:

$$\oint \left(\frac{\delta Q}{T}\right)_{\mathrm{b}} = -\sigma_{\mathrm{cycle}}$$

(Eq. 5.13)

where

$\oint$ indicates integral is to be performed over all parts of the boundary and over the entire cycle.

b subscript indicates integrand is evaluated at the boundary of the system executing the cycle.

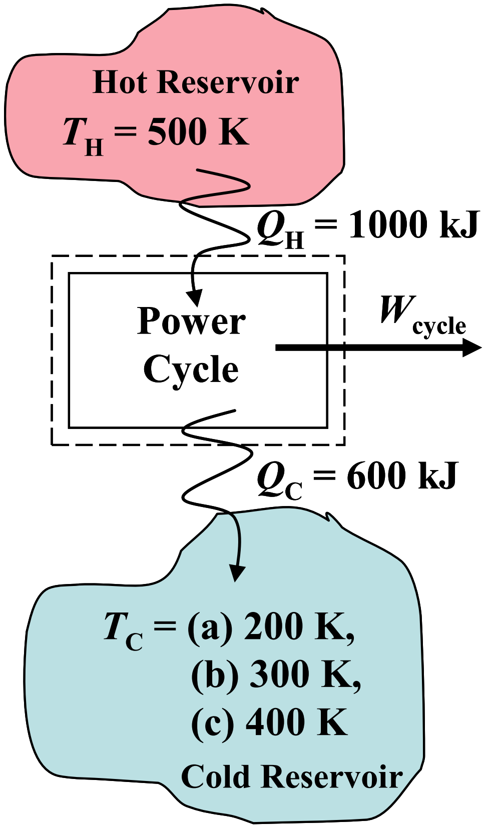
Example: Use of Clausius Inequality

A system undergoes a cycle while receiving 1000 kJ by heat transfer at a temperature of 500 K and discharging 600 kJ by heat transfer at (a) 200 K, (b) 300 K, (c) 400 K. Using Eqs. 5.13 and 5.14, what is the nature of the cycle in each of these cases?

Solution: To determine the nature of the cycle, perform the cyclic integral of Eq. 5.13 to each case and apply Eq. 5.14 to draw a conclusion about the nature of each cycle.

Example: Use of Clausius Inequality

Applying Eq. 5.13 to each cycle: $\oint \left(\frac{\delta Q}{T}\right)_b = \frac{Q_{\text{in}}}{T_H} - \frac{Q_{\text{out}}}{T_C} = -\sigma_{\text{cycle}}$



Example: Use of Clausius Inequality

Applying Eq. 5.13 to each cycle: $\oint \left(\frac{\delta Q}{T}\right)_{\mathrm{b}} = \frac{Q_{\mathrm{in}}}{T_{\mathrm{H}}} - \frac{Q_{\mathrm{out}}}{T_{\mathrm{C}}} = -\sigma_{\mathrm{cycle}}$

(a) $-\sigma_{\mathrm{cycle}} = \frac{1000\ \mathrm{kJ}}{500\ \mathrm{K}} - \frac{600\ \mathrm{kJ}}{200\ \mathrm{K}} = -1\ \mathrm{kJ/K} \rightarrow \boldsymbol{\sigma}_{\mathbf{cycle}} = \mathbf{+1\ kJ/K > 0}$

Irreversibilities present within system

(b) $-\sigma_{\mathrm{cycle}} = \frac{1000\ \mathrm{kJ}}{500\ \mathrm{K}} - \frac{600\ \mathrm{kJ}}{300\ \mathrm{K}} = 0\ \mathrm{kJ/K} \rightarrow \boldsymbol{\sigma}_{\mathbf{cycle}} = \mathbf{0\ kJ/K = 0}$

No irreversibilities present within system

(c) $-\sigma_{\mathrm{cycle}} = \frac{1000\ \mathrm{kJ}}{500\ \mathrm{K}} - \frac{600\ \mathrm{kJ}}{400\ \mathrm{K}} = 0.5\ \mathrm{kJ/K} \rightarrow \boldsymbol{\sigma}_{\mathbf{cycle}} = \mathbf{-0.5\ kJ/K < 0}$

Impossible

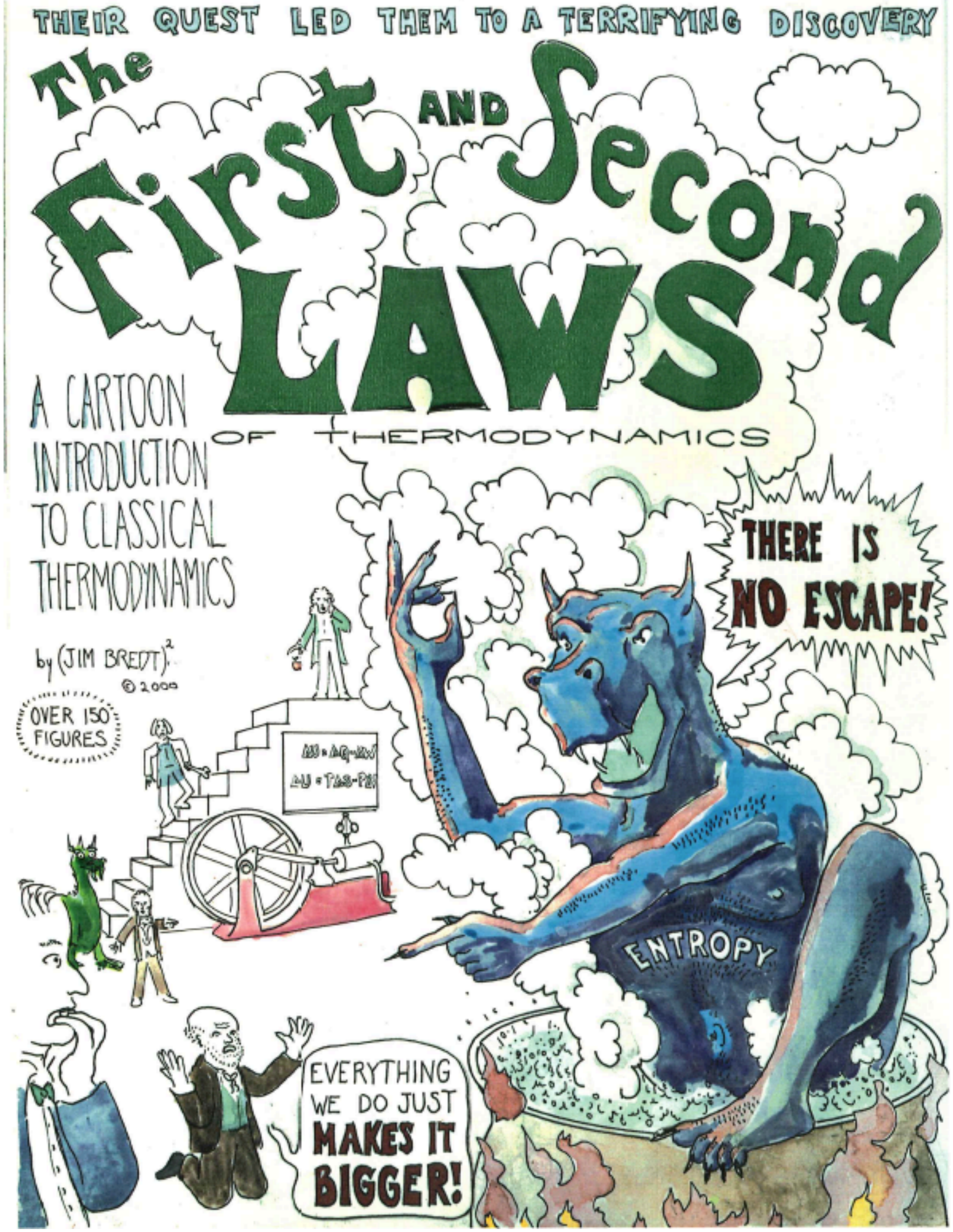
THEIR QUEST LED THEM TO A TERRIFYING DISCOVERY

The First and Second LAWS OF THERMODYNAMICS

A CARTOON INTRODUCTION TO CLASSICAL THERMODYNAMICS

by $(\text{JIM BREDT})^2$

OVER 150 FIGURES



Introducing Entropy Change and the Entropy Balance

- Mass and energy are familiar extensive properties of systems. Entropy is another important extensive property.
- Just as mass and energy are accounted for by mass and energy balances, entropy is accounted for by an entropy balance.
- Like mass and energy, entropy can be transferred across the system boundary.

Introducing Entropy Change and the Entropy Balance

- ►The entropy change and entropy balance concepts are developed using the Clausius inequality expressed as:

$$\oint \left(\frac{\delta Q}{T} \right)_{\mathrm{b}} = -\sigma_{\mathrm{cycle}}$$

(Eq. 5.13)

where

$\sigma_{\mathrm{cycle}} = 0$ **no irreversibilities present within the system**

$\sigma_{\mathrm{cycle}} > 0$ **irreversibilities present within the system**

$\sigma_{\mathrm{cycle}} < 0$ **impossible**

(Eq. 5.14)

Defining Entropy Change

- Recalling (from Sec. 1.3.3) that a quantity is a property if, and only if, its change in value between two states is independent of the process linking the two states, we conclude that the integral represents the change in some property of the system.
- We call this property *entropy* and represent it by ***S***. The change in entropy is

$$S_2 - S_1 = \left(\int_1^2 \frac{\delta Q}{T} \right)_{\substack{\text{int}\\\text{rev}}} \qquad \textbf{(Eq. 6.2a)}$$

where the subscript "int rev" signals that the integral is carried out for any internally reversible process linking states 1 and 2.

Entropy Facts

- Entropy is an extensive property.
- Like any other extensive property, the change in entropy can be positive, negative, or zero:

$$S_2 - S_1: \begin{cases} > 0 \\ = 0 \\ < 0 \end{cases}$$

- By inspection of **Eq. 6.2a**, units for entropy ***S*** are kJ/K and Btu/^{o}R.
- Units for *specific* entropy ***s*** are kJ/kg·K and Btu/lb·^{o}R.

Entropy Facts

► For problem solving, specific entropy values are provided in Tables A-2 through A-18. Values for specific entropy are obtained from these tables using the same procedures as for specific volume, internal energy, and enthalpy, including use of

$$\begin{aligned} s &= (1 - x)s_f + xs_g \\ &= s_f + x(s_g - s_f) \end{aligned}$$

(Eq. 6.4)

for two-phase liquid-vapor mixtures, and

$$s(T, p) \approx s_f(T)$$

(Eq. 6.5)

for liquid water, each of which is similar in form to expressions introduced in Chap. 3 for evaluating $\boldsymbol{v}$, $\boldsymbol{u}$, and $\boldsymbol{h}$.

Entropy and Heat Transfer

- In an internally reversible, adiabatic process (no heat transfer), entropy remains constant. Such a constant-entropy process is called an ***isentropic*** process.
- On rearrangement, **Eq. 6.2b** gives

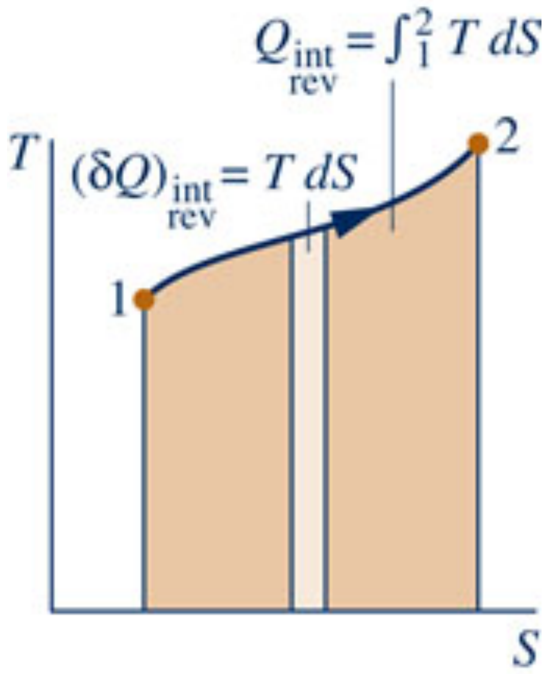
$$(\delta Q)_{\substack{\text{int}\\\text{rev}}} = T\,dS$$

Integrating from state 1 to state 2,

$$Q_{\substack{\text{int}\\\text{rev}}} = \int_1^2 T\,dS \qquad \textbf{(Eq. 6.23)}$$

Entropy and Heat Transfer

From this it follows that an energy transfer by heat to a closed system during an internally reversible process is represented by an area on a temperature-entropy diagram:



Entropy Balance for Closed Systems

- The entropy balance for closed systems can be developed using the Clausius inequality expressed as **Eq. 5.13** and the defining equation for entropy change, **Eq. 6.2a**. The result is

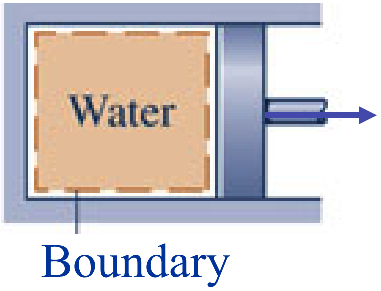
$$\underbrace{S_2 - S_1}_{\substack{\text{entropy}\\ \text{change}}} = \underbrace{\int_1^2 \left(\frac{\delta Q}{T}\right)_b}_{\substack{\text{entropy}\\ \text{transfer}}} + \underbrace{\sigma}_{\substack{\text{entropy}\\ \text{production}}} \qquad \textbf{(Eq. 6.24)}$$

where the subscript **b** indicates the integral is evaluated at the system boundary.

- In accord with the interpretation of σ_{cycle} in the Clausius inequality, **Eq. 5.14**, the value of σ in **Eq. 6.24** adheres to the following interpretation

$$\sigma: \begin{cases} = 0 & \text{(no irreversibilities present within the system)} \\ > 0 & \text{(irreversibilities present within the system)} \\ < 0 & \text{(impossible)} \end{cases}$$

Entropy Balance for Closed Systems



Example: One kg of water vapor contained within a piston-cylinder assembly, initially at 5 bar, 400°C, undergoes an adiabatic expansion to a state where pressure is 1 bar and the temperature is **(a)** 200°C, **(b)** 100°C. Using the entropy balance, determine the nature of the process in each case.

- ► Since the expansion occurs adiabatically, **Eq. 6.24** reduces to give

$$S_2 - S_1 = \cancel{\int_1^2 \left(\frac{\delta Q}{T}\right)_b}^{\,0} + \sigma \;\rightarrow\; m(s_2 - s_1) = \sigma \qquad (1)$$

where $m = 1$ **kg** and **Table A-4** gives $s_1 = 7.7938$ **kJ/kg·K**.

Entropy Balance for Closed Systems

(a) **Table A-4** gives, $s_2 = 7.8343$ kJ/kg·K. Thus **Eq. (1)** gives

$$\sigma = (1 \text{ kg})(7.8343 - 7.7938) \text{ kJ/kg·K} = 0.0405 \text{ kJ/K}$$

Since σ is positive, irreversibilities are present within the system during expansion (a).

(b) **Table A-4** gives, $s_2 = 7.3614$ kJ/kg·K. Thus **Eq. (1)** gives

$$\sigma = (1 \text{ kg})(7.3614 - 7.7938) \text{ kJ/kg·K} = -0.4324 \text{ kJ/K}$$

Since σ is negative, expansion (b) is impossible: it cannot occur *adiabatically*.

Entropy Balance for Closed Systems

More about expansion (b): Considering Eq. 6.24

$$\underbrace{S_2 - S_1}_{\text{entropy change}} = \underbrace{\int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{b}}}_{\text{entropy transfer}} + \underbrace{\sigma}_{\text{entropy production}}$$

$$< 0 \;=\; < 0 \;+\; \geq 0$$

- Since σ cannot be negative and
- For expansion (b) ΔS is negative, then
- By inspection the integral must be negative and so heat transfer *from* the system *must* occur in expansion (b).

Entropy Rate Balance for Closed Systems

- On a time rate basis, the closed system entropy rate balance is

$$\frac{dS}{dt} = \sum_j \frac{\dot{Q}_j}{T_j} + \dot{\sigma} \qquad \textbf{(Eq. 6.28)}$$

where

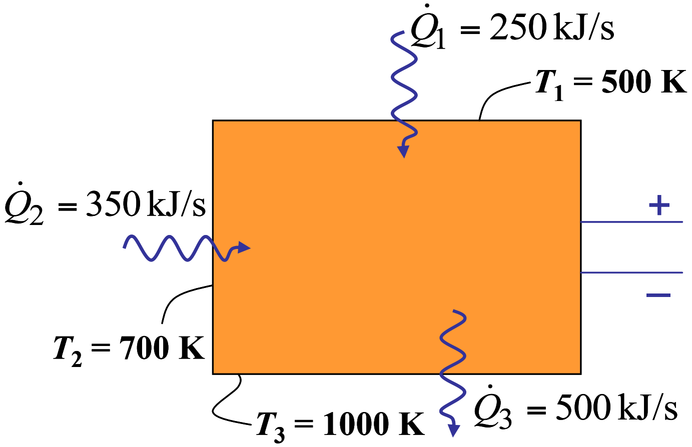
$\frac{dS}{dt}$ = **the time rate of change of the entropy of the system**

$\frac{\dot{Q}_j}{T_j}$ = **the time rate of entropy transfer through the portion of the boundary whose temperature is T_j**

$\dot{\sigma}$ = **time rate of entropy production due to irreversibilities within the system**

Entropy Rate Balance for Closed Systems

Example: An inventor claims that the device shown generates electricity at a rate of 100 kJ/s while *receiving* a heat transfer of energy at a rate of **250 kJ/s** at a temperature of **500 K**, *receiving* a second heat transfer at a rate of **350 kJ/s** at **700 K**, and *discharging* energy by heat transfer at a rate of **500 kJ/s** at a temperature of **1000 K**. Each heat transfer is positive in the direction of the accompanying arrow. For operation at steady state, evaluate this claim.



Entropy Rate Balance for Closed Systems

- Applying an energy rate balance at steady state

$$\cancelto{0}{\frac{dE}{dt}} = 0 = \dot{Q}_1 + \dot{Q}_2 - \dot{Q}_3 - \dot{W}_e$$

Solving $\dot{W}_e = 250\,\text{kJ/s} + 350\,\text{kJ/s} - 500\,\text{kJ/s} = \mathbf{100\,kJ/s}$

The claim is in accord with the first law of thermodynamics.

- Applying an entropy rate balance at steady state

$$\cancelto{0}{\frac{dS}{dt}} = 0 = \frac{\dot{Q}_1}{T_1} + \frac{\dot{Q}_2}{T_2} - \frac{\dot{Q}_3}{T_3} + \dot{\sigma}$$

Solving

$$\dot{\sigma} = -\left(\frac{250\,\text{kJ/s}}{500\,\text{K}} + \frac{350\,\text{kJ/s}}{700\,\text{K}} - \frac{500\,\text{kJ/s}}{1000\,\text{K}}\right)$$

$$\dot{\sigma} = -(0.5 + 0.5 - 0.5)\frac{\text{kJ/s}}{\text{K}} = \mathbf{-0.5\,\frac{kJ/s}{K}}$$

Since σ̇ is negative, the claim is **not** in accord with the second law of thermodynamics and is therefore false.

Entropy Rate Balance for Control Volumes

- Like mass and energy, entropy can be transferred into or out of a control volume by streams of matter.
- Since this is the principal difference between the closed system and control volume entropy rate balances, the control volume form can be obtained by modifying the closed system form to account for such entropy transfer. The result is

$$\underbrace{\frac{dS_{\text{cv}}}{dt}}_{\substack{\text{rate of}\\ \text{entropy}\\ \text{change}}} = \underbrace{\sum_j \frac{\dot{Q}_j}{T_j} + \sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e}_{\substack{\text{rates of}\\ \text{entropy}\\ \text{transfer}}} + \underbrace{\dot{\sigma}_{\text{cv}}}_{\substack{\text{rate of}\\ \text{entropy}\\ \text{production}}} \qquad \textbf{(Eq. 6.34)}$$

where $\dot{m}_i s_i$ and $\dot{m}_e s_e$ account, respectively, for rates of entropy transfer accompanying mass flow at inlets i and exits e.

Entropy Rate Balance for Control Volumes

- ► For control volumes at steady state, **Eq. 6.34** reduces to give

$$0 = \sum_j \frac{\dot{Q}_j}{T_j} + \sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e + \dot{\sigma}_{\mathrm{cv}} \qquad \text{(Eq. 6.36)}$$

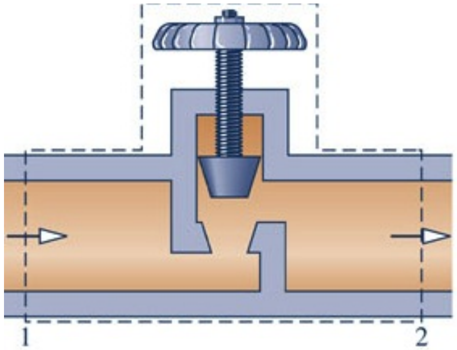
- ► For a one-inlet, one-exit control volume at steady state, **Eq. 6.36** reduces to give

$$0 = \sum_j \frac{\dot{Q}_j}{T_j} + \dot{m}(s_1 - s_2) + \dot{\sigma}_{\mathrm{cv}} \qquad \text{(Eq. 6.37)}$$

where 1 and 2 denote the inlet and exit, respectively, and $\dot{m}$ is the common mass flow rate at these locations.

Entropy Rate Balance for Control Volumes

Example: Water vapor enters a valve at 0.7 bar, 280°C and exits at 0.35 bar. **(a)** If the water vapor undergoes a throttling process, determine the rate of entropy production within the valve, in kJ/K per kg of water vapor flowing. **(b)** What is the source of entropy production in this case?



$p_1 = 0.7$ bar
$T_1 = 280^{o}$C

$p_2 = 0.35$ bar
$h_2 = h_1$

(a) For a throttling process, there is no significant heat transfer. Thus, **Eq. 6.37** reduces to

$$0 = \cancelto{0}{\sum_j \frac{\dot{Q}_j}{T_j}} + \dot{m}(s_1 - s_2) + \dot{\sigma}_{\text{cv}} \rightarrow \quad 0 = \dot{m}(s_1 - s_2) + \dot{\sigma}_{\text{cv}}$$

Entropy Rate Balance for Control Volumes

Solving

$$\frac{\dot{\sigma}_{\text{cv}}}{\dot{m}} = s_2 - s_1$$

From Table A-4, $\boldsymbol{h_1} = \mathbf{3035.0\ kJ/kg}$, $\boldsymbol{s_1} = \mathbf{8.3162\ kJ/kg{\cdot}K}$.

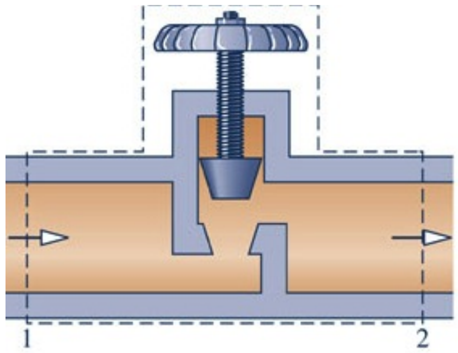
For a throttling process, $\boldsymbol{h_2} = \boldsymbol{h_1}$ (**Eq. 4.22**). Interpolating in Table A-4 at 0.35 bar and $h_2 = 3035.0$ kJ/kg, $\boldsymbol{s_2} = \mathbf{8.6295\ kJ/kg{\cdot}K}$.

Finally $$\frac{\dot{\sigma}_{\text{cv}}}{\dot{m}} = (8.6295 - 8.3162)\ \text{kJ/kg}{\cdot}\text{K} = \mathbf{0.3133\ kJ/kg{\cdot}K}$$

(b) Selecting from the list of irreversibilities provided in **Sec. 5.3.1**, the source of the entropy production here is the *unrestrained* expansion to a lower pressure undergone by the water vapor.

Entropy Rate Balance for Control Volumes

Comment: The value of the entropy production for a single component such as the throttling valve considered here often does not have much significance by itself. The significance of the entropy production of any component is normally determined through comparison with the entropy production values of other components combined with that component to form an integrated system. Reducing irreversibilities of components with the highest entropy production rates may lead to improved thermodynamic performance of the integrated system.



Calculating Entropy Change

- The property data provided in **Tables A-2** through **A-18**, similar compilations for other substances, and numerous important relations among such properties are established using the ***TdS*** equations. When expressed on a unit mass basis, these equations are

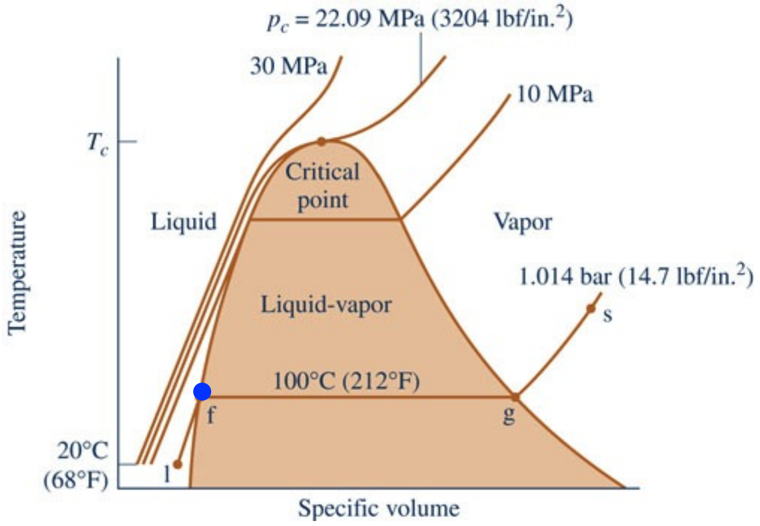
$$T\,ds = du + p\,dv \qquad \textbf{(Eq. 6.10a)}$$

$$T\,ds = dh - v\,dp \qquad \textbf{(Eq. 6.10b)}$$

Calculating Entropy Change

- As an application, consider a change in phase from saturated liquid to saturated vapor at constant pressure.
- Since pressure is constant, **Eq. 6.10b** reduces to give

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



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

$$s_g - s_f = \frac{h_g - h_f}{T} \qquad \textbf{(Eq. 6.12)}$$

This relationship is applied in property tables for tabulating ($s_g - s_f$) from known values of ($h_g - h_f$).

Calculating Entropy Change

►**For example**, consider water vapor at 100°C (373.15 K). From **Table A-2**, $(h_g - h_f) = 2257.1\ \mathrm{kJ/kg}$. **Thus**

$$(s_g - s_f) = (2257.1\ \mathrm{kJ/kg})/373.15\ \mathrm{K} = 6.049\ \mathrm{kJ/kg\cdot K}$$

which agrees with the value from Table A-2, as expected.

►Next, the *TdS* **equations** are applied to two additional cases: substances modeled as incompressible and gases modeled as ideal gases.

Calculating Entropy Change of an Incompressible Substance

- ► The incompressible substance model assumes the specific volume is constant and specific internal energy depends solely on temperature: $u = u(T)$. Thus, $du = c(T)dT$, where c denotes specific heat.
- ► With these relations, **Eq. 6.10a** reduces to give

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

- ► On integration, the change in specific entropy is

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

- ► When the specific heat is constant

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

(Eq. 6.13)

Calculating Entropy Change of an Ideal Gas

- The ideal gas model assumes pressure, specific volume and temperature are related by $pv = RT$. Also, specific internal energy and specific enthalpy each depend solely on temperature: $u = u(T)$, $h = h(T)$, giving $du = c_v dT$ and $dh = c_p dT$, respectively.
- Using these relations and integrating, the ***TdS* equations** give, respectively

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

$$ds = c_v(T)\frac{dT}{T} + R\frac{dv}{v}$$

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

(Eq. 6.17)

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

$$ds = c_p(T)\frac{dT}{T} - R\frac{dp}{p}$$

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

(Eq. 6.18)

Calculating Entropy Change of an Ideal Gas

- ► Since these particular equations give entropy change on a unit of mass basis, the constant ***R*** is determined from $R = \overline{R} / M$.
- ► Since c_v and c_p are functions of temperature for ideal gases, such functional relations are required to perform the integration of the first term on the right of **Eqs. 6.17** and **6.18**.
- ► For several gases modeled as ideal gases, including air, CO_2, CO, O_2, N_2, and water vapor, the evaluation of entropy change can be reduced to a convenient tabular approach using the variable s^o defined by

$$s^\circ(T) = \int_{T'}^{T} \frac{c_p(T)}{T} dT \qquad \textbf{(Eq. 6.19)}$$

where *T*' is an arbitrary reference temperature.

Calculating Entropy Change of an Ideal Gas

- ► Using s^o, the integral term of **Eq. 6.18** can be expressed as

$$\int_{T_1}^{T_2} c_p \frac{dT}{T} = \int_{T'}^{T_2} c_p \frac{dT}{T} - \int_{T'}^{T_1} c_p \frac{dT}{T}$$

$$= s^\circ(T_2) - s^\circ(T_1)$$

- ► Accordingly, **Eq. 6.18** becomes

$$s(T_2, p_2) - s(T_1, p_1) = s^\circ(T_2) - s^\circ(T_1) - R \ln \frac{p_2}{p_1} \qquad \textbf{(Eq. 6.20a)}$$

or on a per mole basis as

$$\bar{s}(T_2, p_2) - \bar{s}(T_1, p_1) = \bar{s}^\circ(T_2) - \bar{s}^\circ(T_1) - \bar{R} \ln \frac{p_2}{p_1} \qquad \textbf{(Eq. 6.20b)}$$

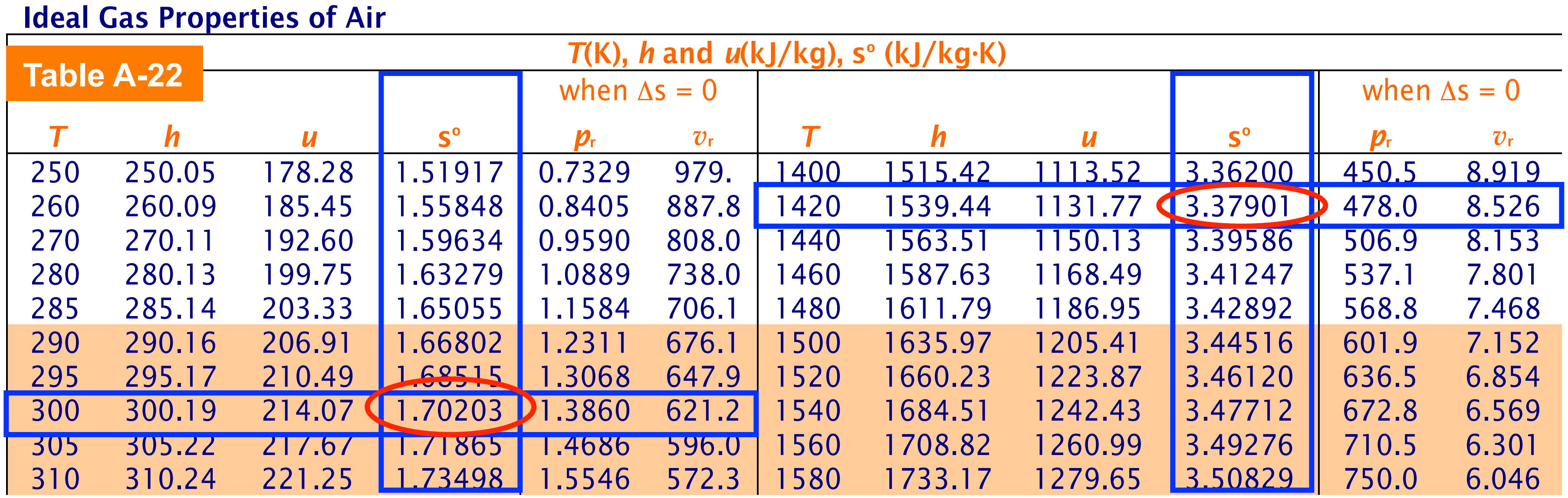
- ► For air, **Tables A-22** and **A-22E** provide s^o in units of kJ/kg·K and Btu/lb·°R, respectively. For the other gases mentioned, **Tables A-23** and **A-23E** provide $\bar{s}^o$ in units of kJ/kmol·K and Btu/lbmol·°R, respectively.

Calculating Entropy Change of an Ideal Gas

Example: Determine the change in specific entropy, in kJ/kg·K, of air as an ideal gas undergoing a process from $T_1 = 300\ \mathrm{K}$, $p_1 = 1\ \mathrm{bar}$ to $T_2 = 1420\ \mathrm{K}$, $p_2 = 5\ \mathrm{bar}$.

► From **Table A-22**, we get $s^o{}_1 = 1.70203$ and $s^o{}_2 = 3.37901$, each in kJ/kg·K. Substituting into **Eq. 6.20a**

$$s_2 - s_1 = (3.37901 - 1.70203)\frac{\mathrm{kJ}}{\mathrm{kg}\cdot\mathrm{K}} - \left(\frac{8.314}{28.97}\right)\left(\frac{\mathrm{kJ}}{\mathrm{kg}\cdot\mathrm{K}}\right)\ln\left(\frac{5\ \mathrm{bar}}{1\ \mathrm{bar}}\right) = 1.215\frac{\mathrm{kJ}}{\mathrm{kg}\cdot\mathrm{K}}$$



Ideal Gas Properties of Air

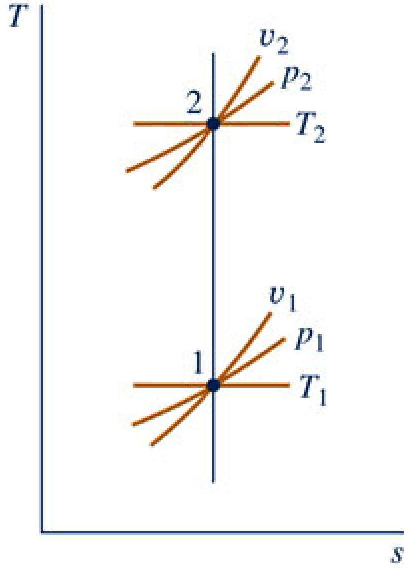
Table A-22

T(K), h and u(kJ/kg), s° (kJ/kg·K)

				when Δs = 0						when Δs = 0	
T	h	u	s°	p_r	v_r	T	h	u	s°	p_r	v_r
250	250.05	178.28	1.51917	0.7329	979.	1400	1515.42	1113.52	3.36200	450.5	8.919
260	260.09	185.45	1.55848	0.8405	887.8	1420	1539.44	1131.77	3.37901	478.0	8.526
270	270.11	192.60	1.59634	0.9590	808.0	1440	1563.51	1150.13	3.39586	506.9	8.153
280	280.13	199.75	1.63279	1.0889	738.0	1460	1587.63	1168.49	3.41247	537.1	7.801
285	285.14	203.33	1.65055	1.1584	706.1	1480	1611.79	1186.95	3.42892	568.8	7.468
290	290.16	206.91	1.66802	1.2311	676.1	1500	1635.97	1205.41	3.44516	601.9	7.152
295	295.17	210.49	1.68515	1.3068	647.9	1520	1660.23	1223.87	3.46120	636.5	6.854
300	300.19	214.07	1.70203	1.3860	621.2	1540	1684.51	1242.43	3.47712	672.8	6.569
305	305.22	217.67	1.71865	1.4686	596.0	1560	1708.82	1260.99	3.49276	710.5	6.301
310	310.24	221.25	1.73498	1.5546	572.3	1580	1733.17	1279.65	3.50829	750.0	6.046

Calculating Entropy Change of an Ideal Gas

- ► **Tables A-22** and **A-22E** provide additional data for air modeled as an ideal gas. These values, denoted by p_r and v_r, refer only to two states having the same specific entropy. This case has important applications, and is shown in the figure.

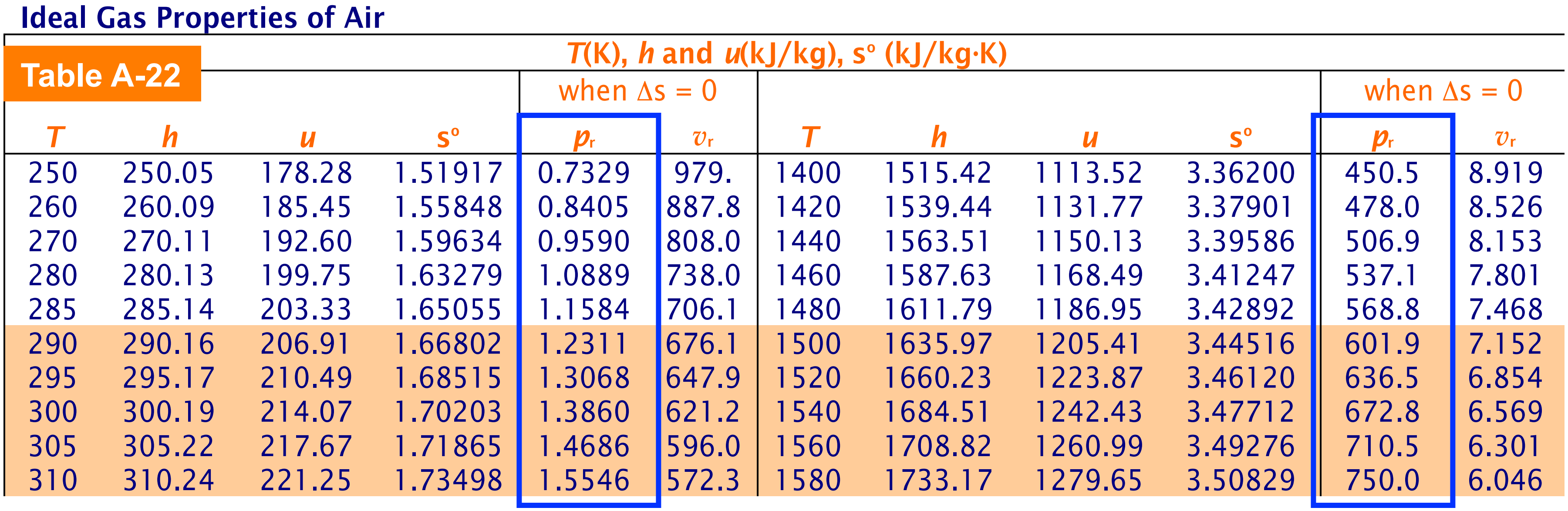


Calculating Entropy Change of an Ideal Gas

- When $s_2 = s_1$, the following equation relates T_1, T_2, p_1, and p_2

$$\frac{p_2}{p_1} = \frac{p_r(T_2)}{p_r(T_1)} \quad (s_1 = s_2, \text{ air only}) \qquad \textbf{(Eq. 6.41)}$$

where $p_r(T)$ is read from Table A-22 or A-22E, as appropriate.



Ideal Gas Properties of Air

Table A-22

T(K), h and u(kJ/kg), s° (kJ/kg·K)

T	h	u	s°	p_r (when Δs = 0)	v_r (when Δs = 0)	T	h	u	s°	p_r (when Δs = 0)	v_r (when Δs = 0)
250	250.05	178.28	1.51917	0.7329	979.	1400	1515.42	1113.52	3.36200	450.5	8.919
260	260.09	185.45	1.55848	0.8405	887.8	1420	1539.44	1131.77	3.37901	478.0	8.526
270	270.11	192.60	1.59634	0.9590	808.0	1440	1563.51	1150.13	3.39586	506.9	8.153
280	280.13	199.75	1.63279	1.0889	738.0	1460	1587.63	1168.49	3.41247	537.1	7.801
285	285.14	203.33	1.65055	1.1584	706.1	1480	1611.79	1186.95	3.42892	568.8	7.468
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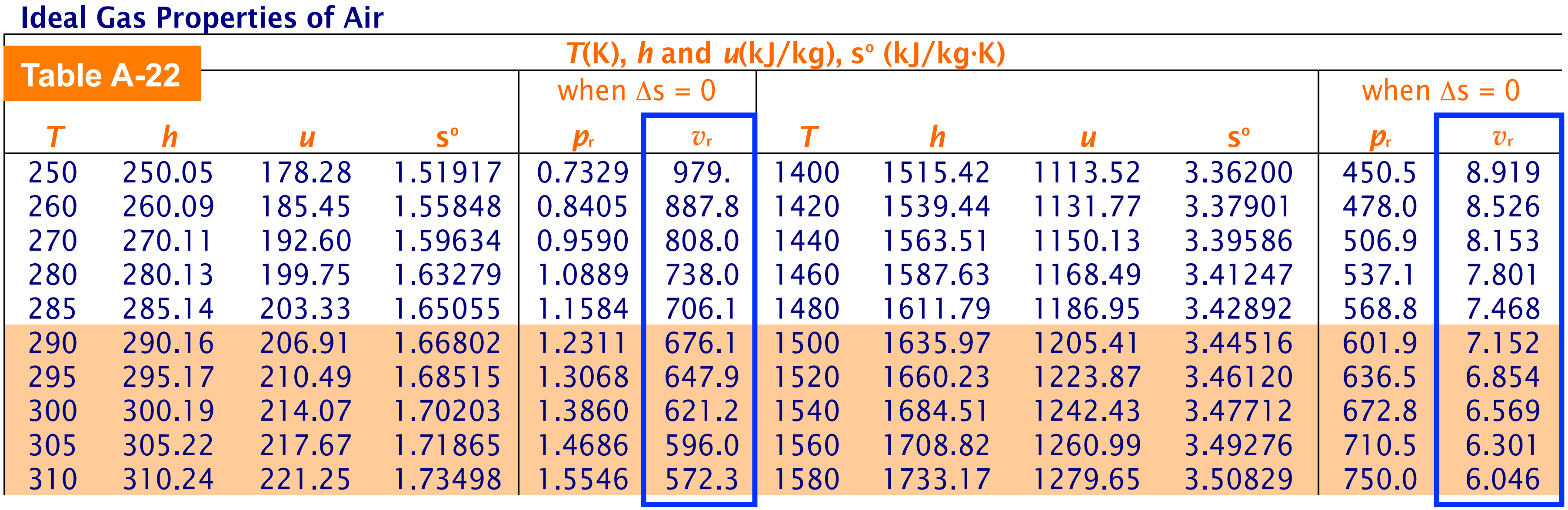
305	305.22	217.67	1.71865	1.4686	596.0	1560	1708.82	1260.99	3.49276	710.5	6.301
310	310.24	221.25	1.73498	1.5546	572.3	1580	1733.17	1279.65	3.50829	750.0	6.046

Calculating Entropy Change of an Ideal Gas

- When $s_2 = s_1$, the following equation relates T_1, T_2, v_1, and v_2

$$\frac{v_2}{v_1} = \frac{v_r(T_2)}{v_r(T_1)} \qquad (s_1 = s_2, \text{ air only}) \qquad \textbf{(Eq. 6.42)}$$

where $v_r(T)$ is read from Table A-22 or A-22E, as appropriate.



Ideal Gas Properties of Air

Table A-22

T(K), h and u(kJ/kg), s° (kJ/kg·K)

				when Δs = 0						when Δs = 0	
T	h	u	$s°$	p_r	v_r	T	h	u	$s°$	p_r	v_r
250	250.05	178.28	1.51917	0.7329	979.	1400	1515.42	1113.52	3.36200	450.5	8.919
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280	280.13	199.75	1.63279	1.0889	738.0	1460	1587.63	1168.49	3.41247	537.1	7.801
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310	310.24	221.25	1.73498	1.5546	572.3	1580	1733.17	1279.65	3.50829	750.0	6.046

Entropy Change of an Ideal Gas Assuming Constant Specific Heats

- ► When the specific heats c_v and c_p are assumed constant, **Eqs. 6.17** and **6.18** reduce, respectively, to

(Eq. 6.17)

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

$$\downarrow$$

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

(Eq. 6.21)

(Eq. 6.18)

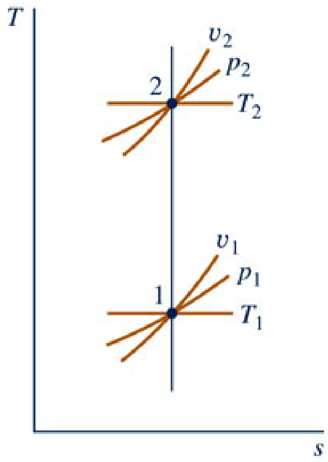
$$s(T_2, p_2) - s(T_1, p_1) = \int_{T_1}^{T_2} c_p(T)\frac{dT}{T} - R\ln\frac{p_2}{p_1}$$

$$\downarrow$$

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

(Eq. 6.22)

- ► These expressions have many applications. In particular, they can be applied to develop relations among T, p, and v at two states having the same specific entropy as shown in the figure.



Entropy Change of an Ideal Gas Assuming Constant Specific Heats

- Since $s_2 = s_1$, **Eqs. 6.21** and **6.22** become

$$0 = c_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1}$$

$$0 = c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$

- With the ideal gas relations

where k is the specific ratio

$$c_p(T) = \frac{kR}{k-1} \qquad c_v(T) = \frac{R}{k-1}$$

- These equations can be solved, respectively, to give

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{(k-1)/k} \qquad (s_1 = s_2, \text{constant } k)$$

(Eq. 6.43)

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1} \qquad (s_1 = s_2, \text{constant } k)$$

(Eq. 6.44)

- Eliminating the temperature ratio gives

$$\frac{p_2}{p_1} = \left(\frac{v_1}{v_2}\right)^{k} \qquad (s_1 = s_2, \text{constant } k)$$

(Eq. 6.45)

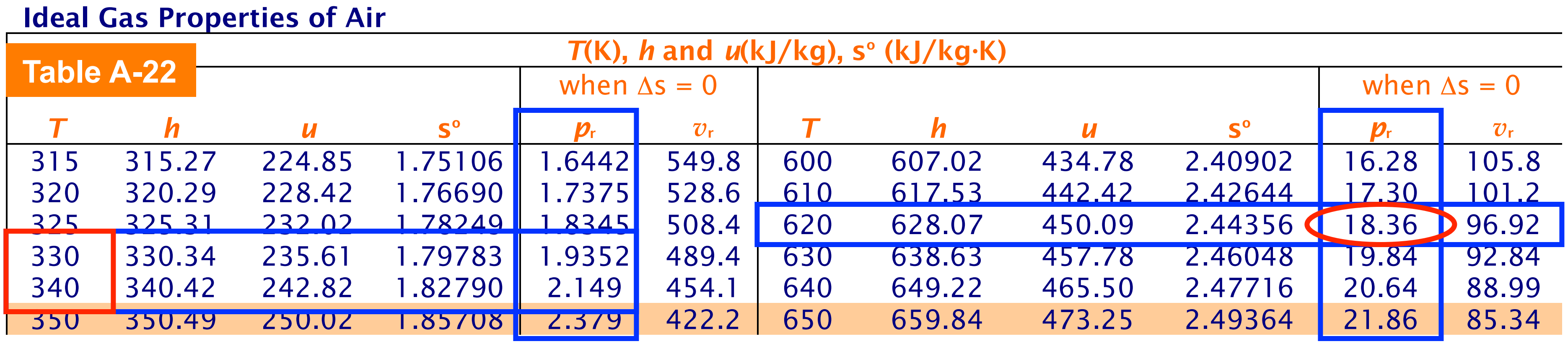
Calculating Entropy Change of an Ideal Gas

Example: Air undergoes a process from $T_1 = 620$ K, $p_1 = 12$ bar to a final state where $s_2 = s_1$, $p_2 = 1.4$ bar. Employing the ideal gas model, determine the final temperature T_2, in K. Solve using **(a)** p_r data from Table A-22 and **(b)** a constant specific heat ratio k evaluated at 620 K from Table A-20: k **= 1.374**. Comment.

(a) With **Eq. 6.41** and $p_r(T_1) = 18.36$ from Table A-22

$$p_r(T_2) = p_r(T_1)\left(\frac{p_2}{p_1}\right) = 18.36\left(\frac{1.4\text{ bar}}{12\text{ bar}}\right) = 2.142$$

Interpolating in Table A-22, $T_2 = 339.7$ K



Ideal Gas Properties of Air

Table A-22

T(K), *h* and *u*(kJ/kg), s° (kJ/kg·K)

				when Δs = 0						when Δs = 0	
T	*h*	*u*	s°	p_r	v_r	*T*	*h*	*u*	s°	p_r	v_r
315	315.27	224.85	1.75106	1.6442	549.8	600	607.02	434.78	2.40902	16.28	105.8
320	320.29	228.42	1.76690	1.7375	528.6	610	617.53	442.42	2.42644	17.30	101.2
325	325.31	232.02	1.78249	1.8345	508.4	620	628.07	450.09	2.44356	18.36	96.92
330	330.34	235.61	1.79783	1.9352	489.4	630	638.63	457.78	2.46048	19.84	92.84
340	340.42	242.82	1.82790	2.149	454.1	640	649.22	465.50	2.47716	20.64	88.99
350	350.49	250.02	1.85708	2.379	422.2	650	659.84	473.25	2.49364	21.86	85.34

Calculating Entropy Change of an Ideal Gas

(b) With **Eq. 6.43**

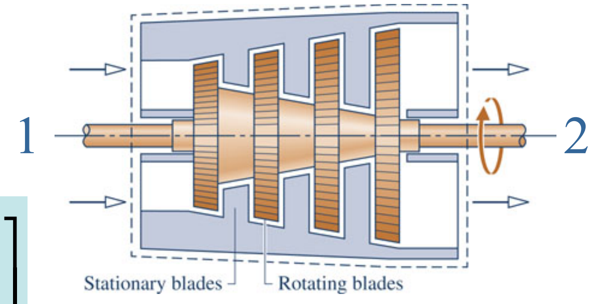
$$T_2 = T_1\left(\frac{p_2}{p_1}\right)^{(k-1)/k} = 620\ \text{K}\left(\frac{1.4\ \text{bar}}{12\ \text{bar}}\right)^{(0.374/1.374)}$$

$$\boldsymbol{T_2 = 345.5\ \text{K}}$$

Comment: The approach of **(a)** accounts for variation of specific heat with temperature but the approach of **(b)** does not. With a ***k*** value more representative of the temperature interval, the value obtained in **(b)** using **Eq. 6.43** would be in better agreement with that obtained in **(a)** with **Eq. 6.41**.

Isentropic Turbine Efficiency

- For a turbine, the energy rate balance reduces to



$$0 = \cancel{\dot{Q}_{\text{cv}}} - \dot{W}_{\text{cv}} + \dot{m}\left[(h_1 - h_2) + \cancel{\frac{(V_1^2 - V_2^2)}{2}} + \cancel{g(z_1 - z_2)}\right]$$

- **If the change in kinetic energy of flowing matter is negligible, $\frac{1}{2}(V_1^2 - V_2^2)$ drops out.**
- **If the change in potential energy of flowing matter is negligible, $g(z_1 - z_2)$ drops out.**
- **If the heat transfer with surroundings is negligible, $\dot{Q}_{\text{cv}}$ drops out.**

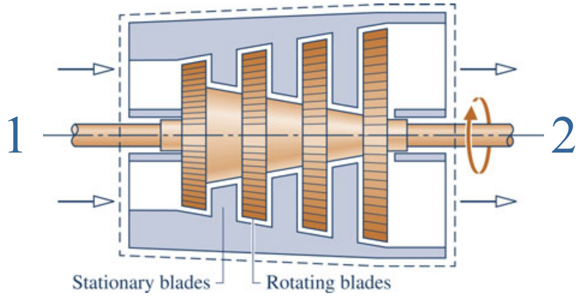
$$\frac{\dot{W}_{\text{cv}}}{\dot{m}} = h_1 - h_2$$

where

the left side is work *developed* per unit of mass flowing.

Isentropic Turbine Efficiency

- For a turbine, the entropy rate balance reduces to

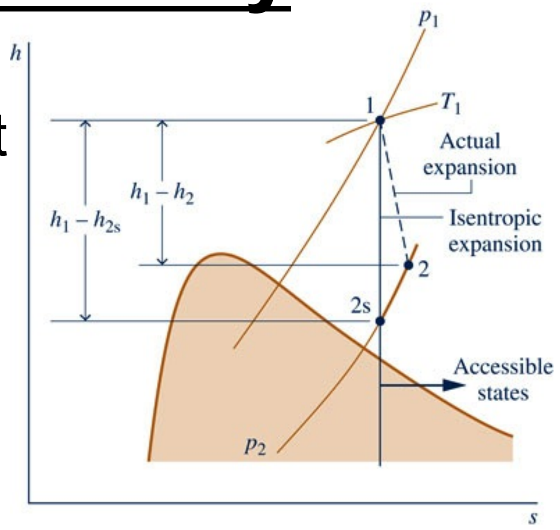


$$0 = \cancel{\sum_j \frac{\dot{Q}_j}{T_j}} + \dot{m}(s_1 - s_2) + \dot{\sigma}_{cv}$$

- If the heat transfer with surroundings is negligible, $\dot{Q}_j$ drops out.

$$\frac{\dot{\sigma}_{cv}}{\dot{m}} = s_2 - s_1 \geq 0$$

Isentropic Turbine Efficiency



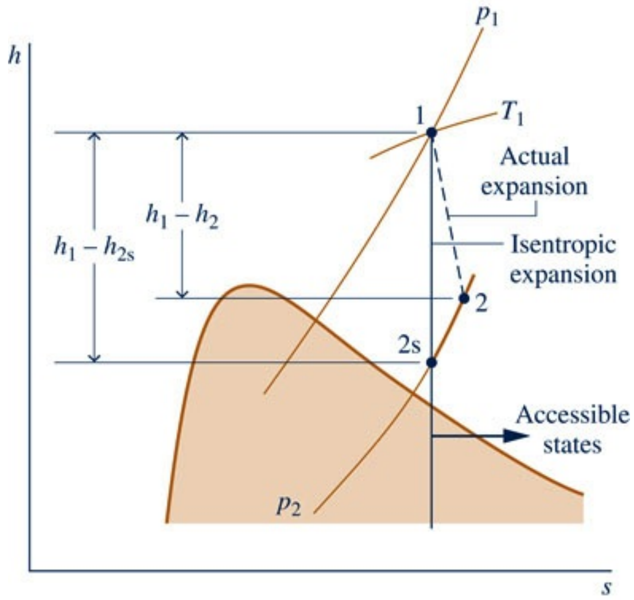
- Since the rate of entropy production cannot be negative, the only turbine exit states that can be attained in an ***adiabatic*** expansion are those with $s_2 \geq s_1$. This is shown on the Mollier diagram to the right.

- The state labeled **2s** on the figure would be attained only in an isentropic expansion from the inlet state to the specified exit pressure – that is, **2s** would be attained only in the absence of internal irreversibilities. By inspection of the figure, the maximum theoretical value for the turbine work per unit of mass flowing is developed in such an internally reversible, adiabatic expansion:

$$\left(\frac{\dot{W}_{\mathrm{cv}}}{\dot{m}}\right)_{\mathrm{s}} = h_1 - h_{2\mathrm{s}}$$

Isentropic Turbine Efficiency

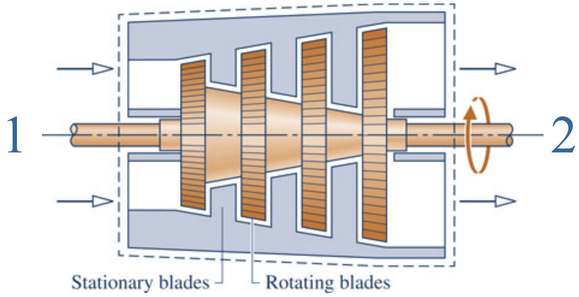
- The isentropic turbine efficiency is the ratio of the actual turbine work to the maximum theoretical work, each per unit of mass flowing:



$$\eta_t = \frac{\dot{W}_{cv}/\dot{m}}{(\dot{W}_{cv}/\dot{m})_s} = \frac{h_1 - h_2}{h_1 - h_{2s}}$$

(Eq. 6.46)

Isentropic Turbine Efficiency



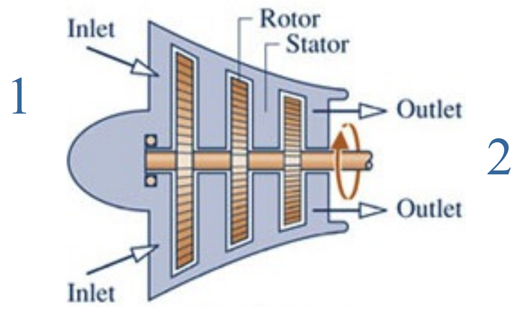
Example: Water vapor enters a turbine at $p_1 = 5$ bar, $T_1 = 320^{\circ}$C and exits at $p_2 = 1$ bar. The work developed is measured as **271 kJ per kg** of water vapor flowing. Applying **Eq. 6.46**, determine the isentropic turbine efficiency.

► From Table A-4, $h_1 = 3105.6$ kJ/kg, $s_1 = 7.5308$ kJ/kg. With $s_{2s} = s_1$, interpolation in Table A-4 at a pressure of 1 bar gives $h_{2s} = 2743.0$ kJ/kg. Substituting values into **Eq. 6.46**

$$\eta_{\mathrm{t}} = \frac{\dot{W}_{\mathrm{cv}}/\dot{m}}{h_1 - h_{2\mathrm{s}}} = \frac{271\,\mathrm{kJ/kg}}{(3105.6 - 2743.0)\,\mathrm{kJ/kg}} = 0.75\,(75\%)$$

Isentropic Compressor and Pump Efficiencies

- For a compressor the energy rate balance reduces to



$$0 = \cancel{\dot{Q}_{\text{cv}}} - \dot{W}_{\text{cv}} + \dot{m}\left[(h_1 - h_2) + \cancel{\frac{(V_1^2 - V_2^2)}{2}} + \cancel{g(z_1 - z_2)}\right]$$

- **If the change in kinetic energy of flowing matter is negligible, $\frac{1}{2}(V_1^2 - V_2^2)$ drops out.**
- **If the change in potential energy of flowing matter is negligible, $g(z_1 - z_2)$ drops out.**
- **If the heat transfer with surroundings is negligible, $\dot{Q}_{\text{cv}}$ drops out.**

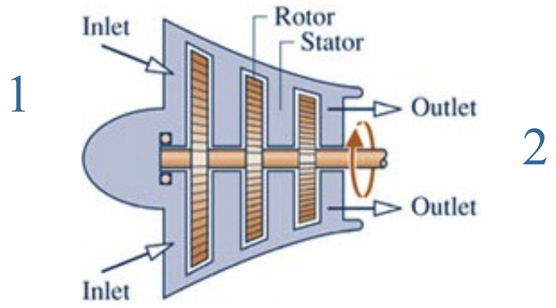
$$\left(-\frac{\dot{W}_{\text{cv}}}{\dot{m}}\right) = h_2 - h_1$$

where

the left side is work *input* per unit of mass flowing.

Isentropic Compressor and Pump Efficiencies

- For a compressor the entropy rate balance reduces to

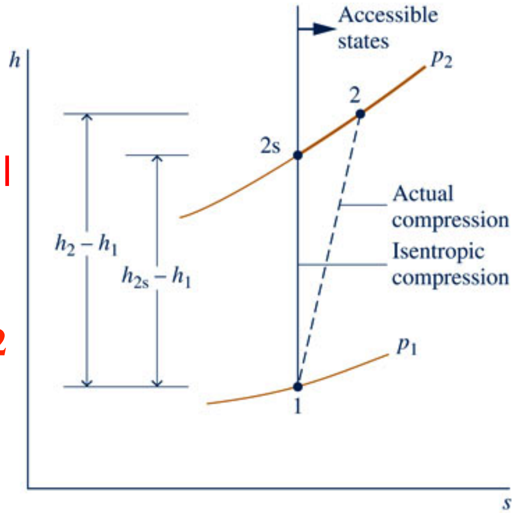


$$0 = \cancel{\sum_j \frac{\dot{Q}_j}{T_j}} + \dot{m}(s_1 - s_2) + \dot{\sigma}_{\mathrm{cv}}$$

- If the heat transfer with surroundings is negligible, $\dot{Q}_j$ drops out.

$$\frac{\dot{\sigma}_{\mathrm{cv}}}{\dot{m}} = s_2 - s_1 \geq 0$$

Isentropic Compressor and Pump Efficiencies

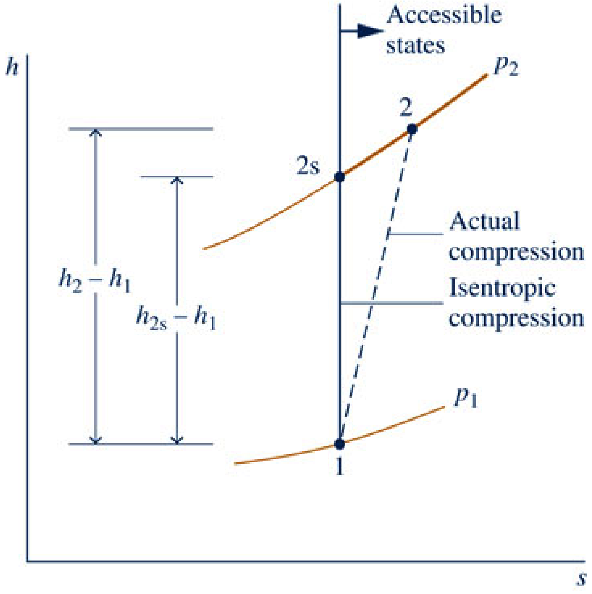


- Since the rate of entropy production cannot be negative, the only compressor exit states that can be attained in an ***adiabatic*** compression are those with $s_2 \geq s_1$. This is shown on the Mollier diagram to the right.
- The state labeled **2s** on the figure would be attained only in an isentropic compression from the inlet state to the specified exit pressure – that is, state **2s** would be attained only in the absence of internal irreversibilities. By inspection of the figure, the minimum theoretical value for the compressor work input per unit of mass flowing is for such an internally reversible, adiabatic compression:

$$\left(-\frac{\dot{W}_{\text{cv}}}{\dot{m}}\right)_{\text{s}} = h_{2\text{s}} - h_1$$

Isentropic Compressor and Pump Efficiencies

- ►The isentropic compressor efficiency is the ratio of the minimum theoretical work input to the actual work input, each per unit of mass flowing:



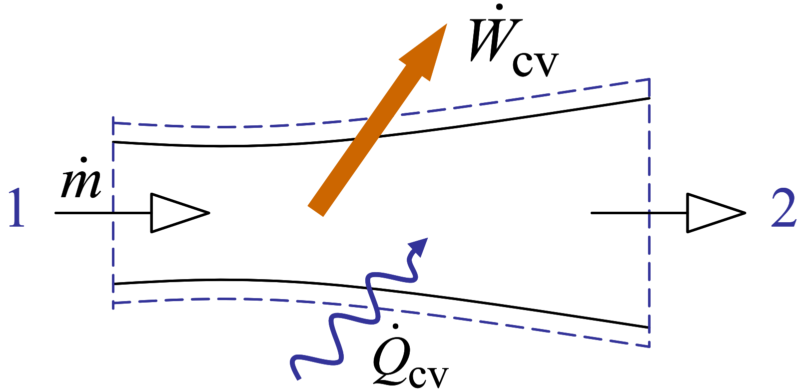
$$\eta_c = \frac{(-\dot{W}_{cv}/\dot{m})_s}{(-\dot{W}_{cv}/\dot{m})} = \frac{h_{2s} - h_1}{h_2 - h_1}$$

(Eq. 6.48)

- ►An isentropic pump efficiency is defined similarly.

Heat Transfer and Work in Internally Reversible Steady-State Flow Processes

- Consider a one-inlet, one-exit control volume at steady state:



- Compressors, pumps, and other devices commonly encountered in engineering practice are included in this class of control volumes.
- The objective is to introduce expressions for the heat transfer rate $\dot{Q}_{cv}/\dot{m}$ and work rate $\dot{W}_{cv}/\dot{m}$ in the absence of internal irreversibilities. The resulting expressions have important applications.

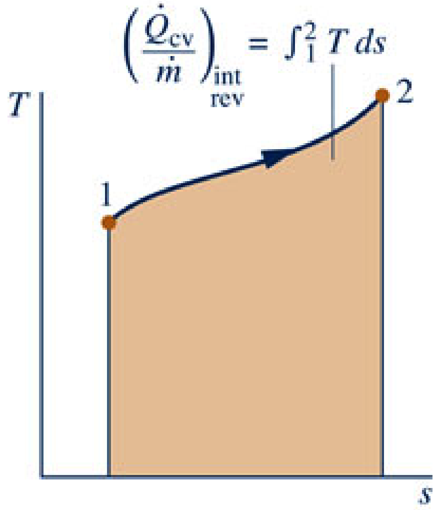
Heat Transfer and Work in Internally Reversible Steady-State Flow Processes

- In agreement with the discussion of energy transfer by heat to a closed system during an internally reversible process (Sec. 6.6.1), in the present application we have

$$\left(\frac{\dot{Q}_{\mathrm{cv}}}{\dot{m}}\right)_{\substack{\mathrm{int}\\ \mathrm{rev}}} = \int_1^2 T\,ds \qquad \textbf{(Eq. 6.49)}$$

where the subscript "**int rev**" signals that the expression applies only in the absence of internal irreversibilities.

- As shown by the figure, when the states visited by a unit mass passing from inlet to exit without internal irreversibilities are described by a curve on a *T-s* diagram, the heat transfer per unit of mass flowing is represented by the area under the curve.



Heat Transfer and Work in Internally Reversible Steady-State Flow Processes

- Neglecting kinetic and potential energy effects, an energy rate balance for the control volume reduces to

$$\left(\frac{\dot{W}_{\mathrm{cv}}}{\dot{m}}\right)_{\substack{\mathrm{int}\\ \mathrm{rev}}} = \left(\frac{\dot{Q}_{\mathrm{cv}}}{\dot{m}}\right)_{\substack{\mathrm{int}\\ \mathrm{rev}}} + (h_1 - h_2) + \cancel{\left(\frac{\mathrm{V}_1^2 - \mathrm{V}_2^2}{2}\right)} + g\cancel{(z_1 - z_2)}$$

- With **Eq. 6.49**, this becomes $\left(\frac{\dot{W}_{\mathrm{cv}}}{\dot{m}}\right)_{\substack{\mathrm{int}\\ \mathrm{rev}}} = \int_1^2 T\,ds + (h_1 - h_2)$ **(1)**

- Since internal irreversibilities are assumed absent, each unit of mass visits a sequence of equilibrium states as it passes from inlet to exit. Entropy, enthalpy, and pressure changes are therefore related by the ***TdS*** equation, **Eq. 6.10b**:

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

Heat Transfer and Work in Internally Reversible Steady-State Flow Processes

- Integrating from inlet to exit: $\int_1^2 T\,ds = (h_2 - h_1) - \int_1^2 v\,dp$

- With this relation **Eq. (1)** becomes

$$\left(\frac{\dot{W}_{\text{cv}}}{\dot{m}}\right)_{\substack{\text{int}\\ \text{rev}}} = -\int_1^2 v\,dp$$

(Eq. 6.51b)

- If the specific volume remains approximately constant, as in many applications with liquids, **Eq. 6.51b** becomes

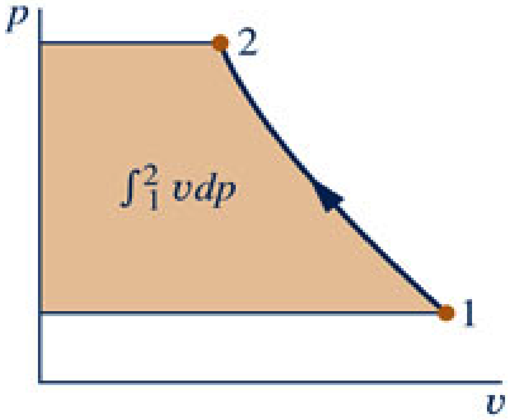
$$\left(\frac{\dot{W}_{\text{cv}}}{\dot{m}}\right)_{\substack{\text{int}\\ \text{rev}}} = -v(p_2 - p_1)$$

(Eq. 6.51c)

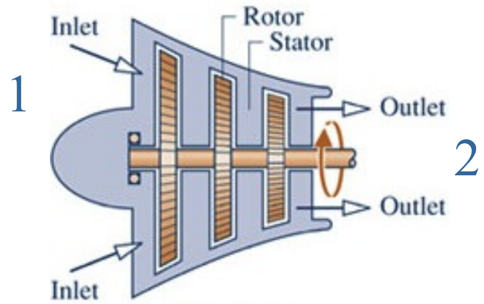
This is applied in the discussion of vapor power cycles in Chapter 8.

Heat Transfer and Work in Internally Reversible Steady-State Flow Processes

- As shown by the figure, when the states visited by a unit mass passing from inlet to exit without internal irreversibilities are described by a curve on a ***p-v*** diagram, the *magnitude* of $\int vdp$ is shown by the area *behind* the curve.



Heat Transfer and Work in Internally Reversible Steady-State Flow Processes



Example: A compressor operates at steady state with natural gas entering at at p_1, v_1. The gas undergoes a polytropic process described by $pv = constant$ and exits at a higher pressure, p_2.

(a) Ignoring kinetic and potential energy effects, evaluate the work per unit of mass flowing.

(b) If internal irreversibilities were present, would the magnitude of the work per unit of mass flowing be less than, the same as, or greater than determined in part (a)?

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(a) With ***pv = constant***, **Eq. 6.51b** gives

$$\left(\frac{\dot{W}_{\text{cv}}}{\dot{m}}\right)_{\substack{\text{int}\\ \text{rev}}} = -\int_1^2 v\,dp = -constant\int_1^2 \frac{dp}{p}$$

$$= -(p_1 v_1)\ln(p_2/p_1) \qquad (\text{polytropic}, n = 1)$$

The minus sign indicates that the compressor requires a work ***input***.

(b) Left for class discussion.