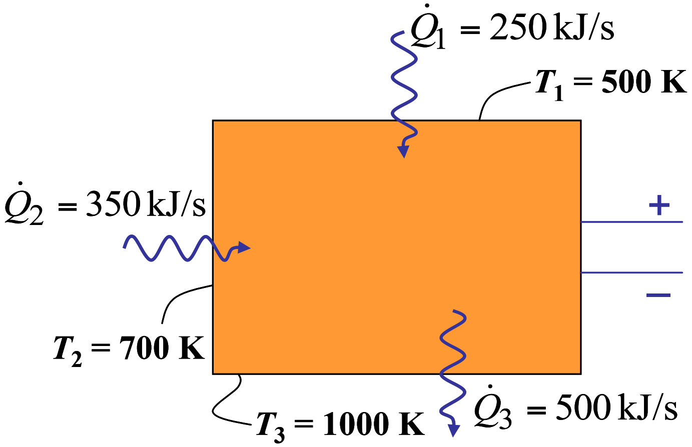
Entropy Rate Balance for Closed Systems

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 $\dot{\sigma}$ 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

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

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

$$0 = \sum_j \frac{\dot{Q}_j}{T_j} + \sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e + \dot{\sigma}_{\mathrm{cv}}$$

(Eq. 6.36)

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

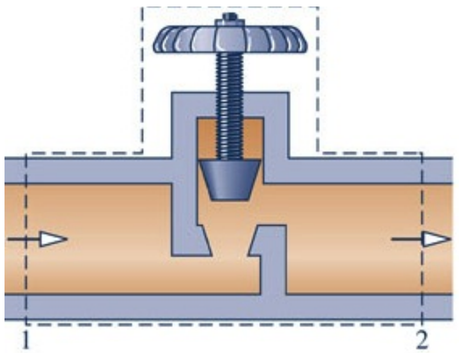
$$0 = \sum_j \frac{\dot{Q}_j}{T_j} + \dot{m}(s_1 - s_2) + \dot{\sigma}_{\mathrm{cv}}$$

(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?



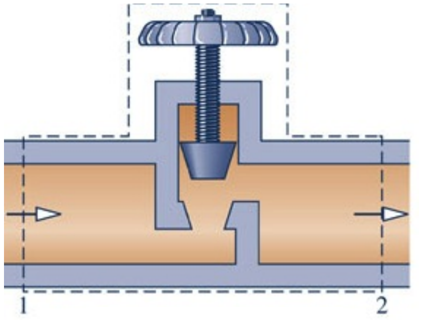
$p_1 = 0.7$ bar
$T_1 = 280$°C

$p_2 = 0.35$ 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



p_1 = 0.7 bar
T_1 = 280°C

p_2 = 0.35 bar
$h_2 = h_1$

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

From Table A-4, h_1 = **3035.0 kJ/kg**, s_1 = **8.3162 kJ/kg·K**.

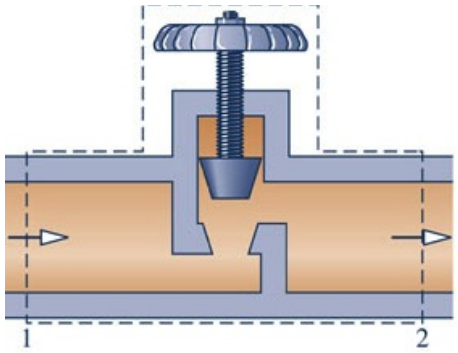
For a throttling process, $h_2 = h_1$ (**Eq. 4.22**). Interpolating in Table A-4 at 0.35 bar and h_2 = 3035.0 kJ/kg, s_2 = **8.6295 kJ/kg·K**.

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

(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

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

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

$$T\,ds = du + p\,dv$$ **(Eq. 6.10a)**

$$T\,ds = dh - v\,dp$$ **(Eq. 6.10b)**

$$T\,ds = du + p\,dv$$ **(Eq. 6.10a)**

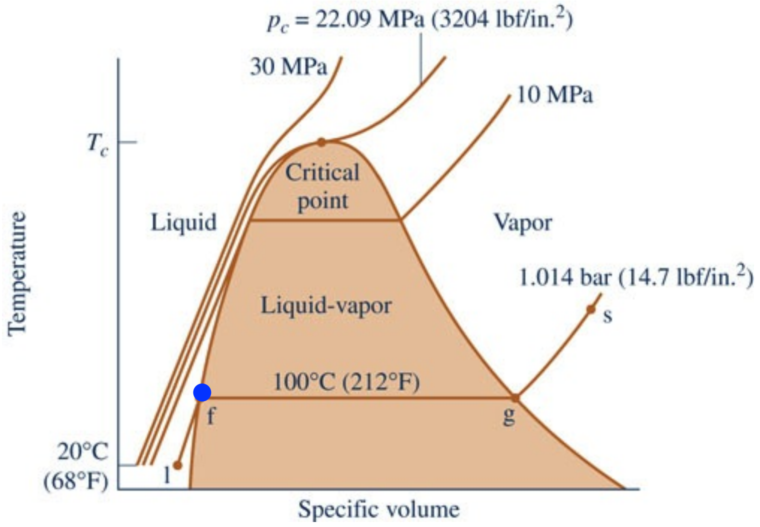
$$T\,ds = dh - v\,dp$$ **(Eq. 6.10b)**

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

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

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

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

- 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

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

(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

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

(Eq. 6.20a)

or on a per mole basis as

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

(Eq. 6.20b)

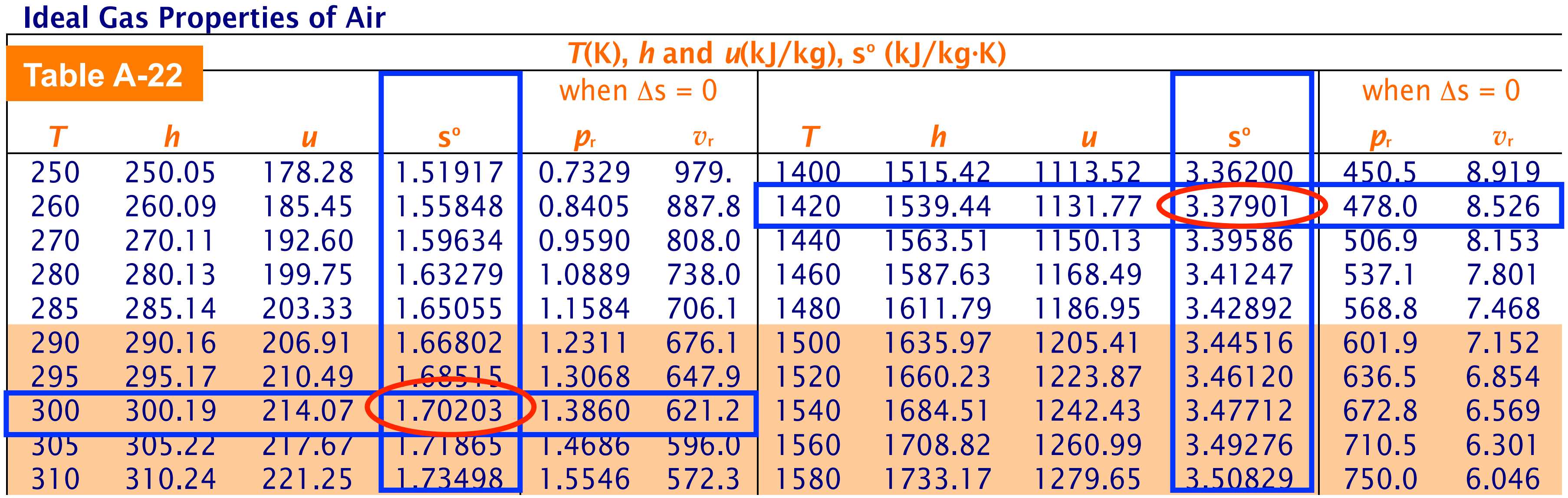
- For air, **Tables A-22** and **A-22E** provide s^o in units of kJ/kg·K and Btu/lb·°R, respectively. For the other gases mentioned, **Tables A-23** and **A-23E** provide $\bar{s}^o$ in units of kJ/kmol·K and Btu/lbmol·°R, respectively.

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 $s^{\mathrm{o}}_1 = 1.70203$ and $s^{\mathrm{o}}_2 = 3.37901$, 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

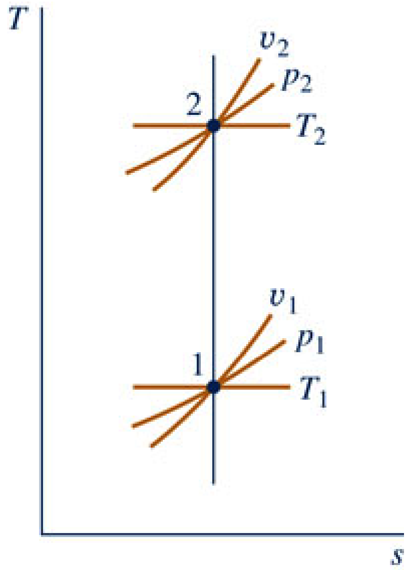
Table A-22

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.



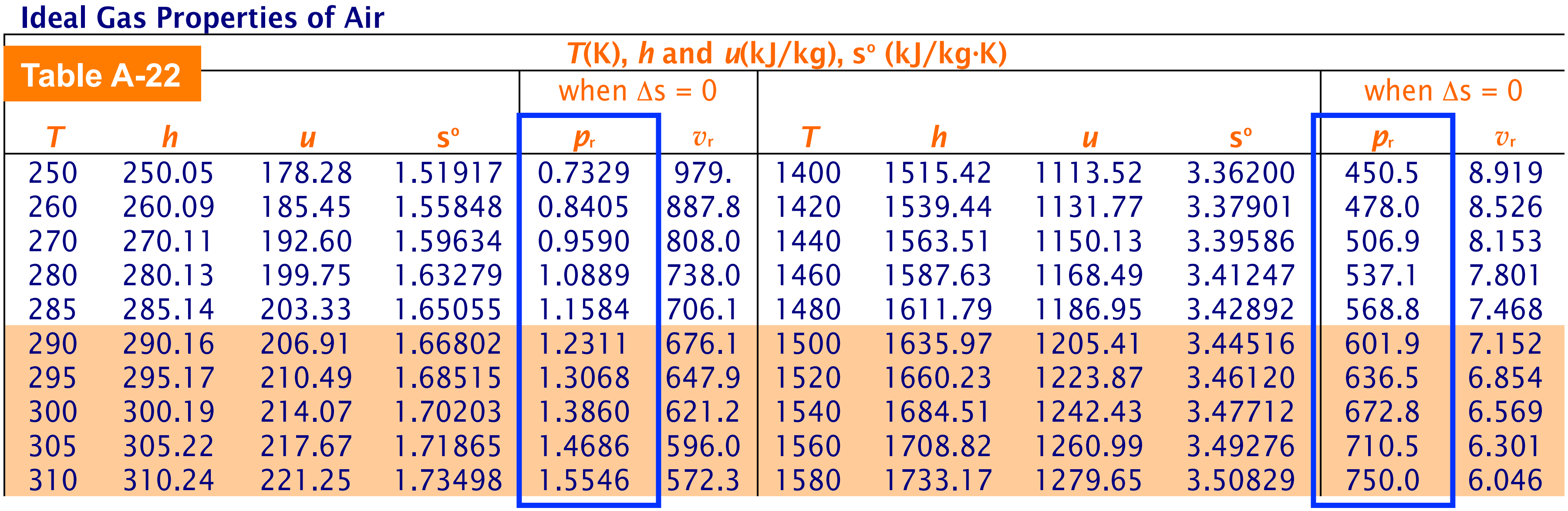
Calculating Entropy Change of an Ideal Gas

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

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

(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)											
				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

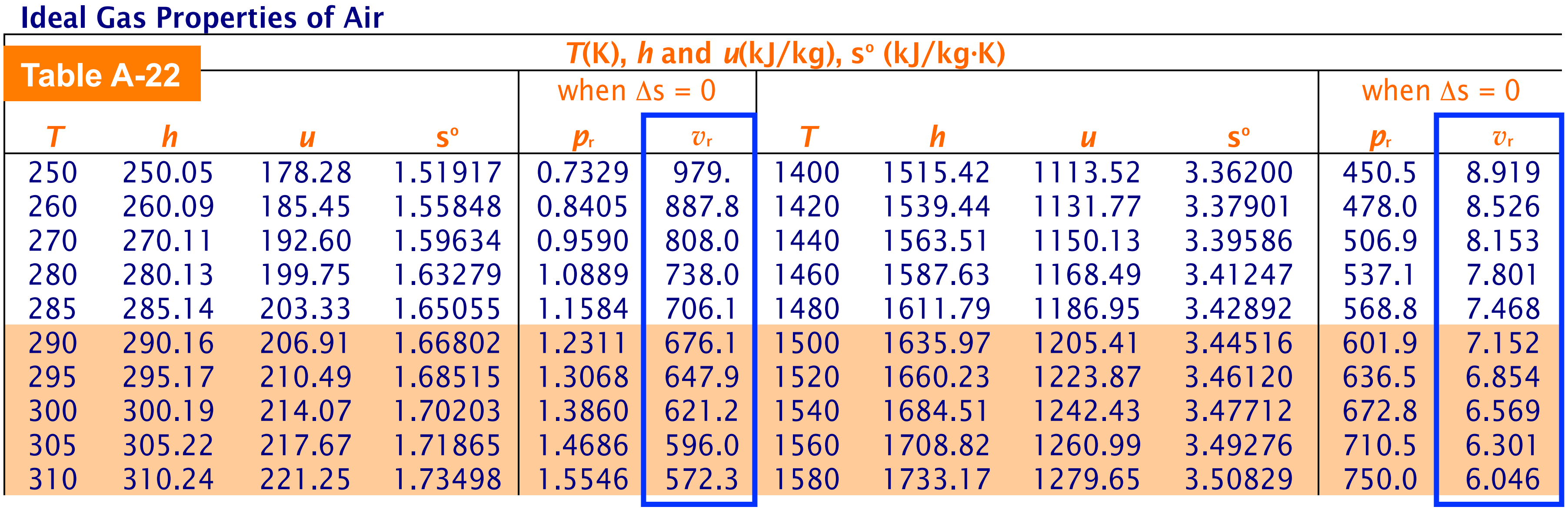
Calculating Entropy Change of an Ideal Gas

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

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

(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
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

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)

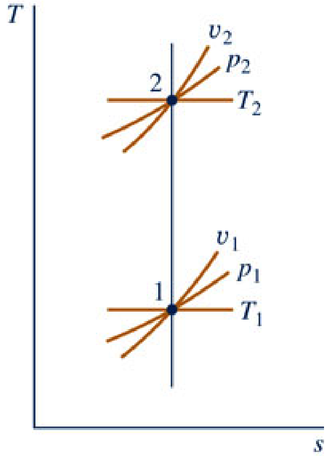
$$s(T_2, p_2) - s(T_1, p_1) = \int_{T_1}^{T_2} c_p(T)\frac{dT}{T} - R\ln\frac{p_2}{p_1}$$

$$\downarrow$$

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

(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

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

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

- 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)

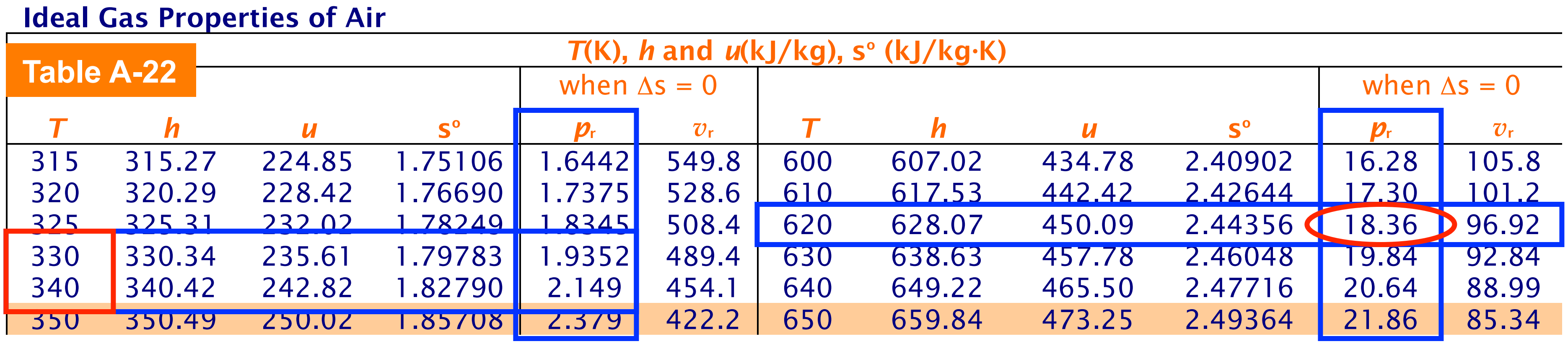
Calculating Entropy Change of an Ideal Gas

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**

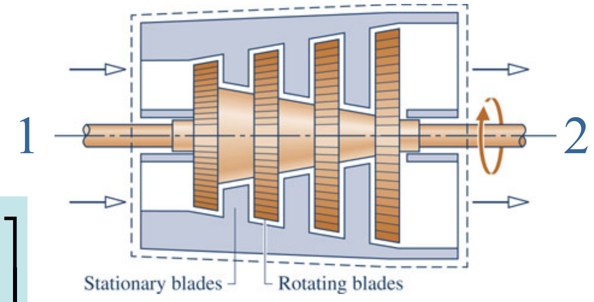
$$T_2 = T_1\left(\frac{p_2}{p_1}\right)^{(k-1)/k} = 620\,\mathrm{K}\left(\frac{1.4\ \mathrm{bar}}{12\ \mathrm{bar}}\right)^{(0.374/1.374)}$$

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

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



$$0 = \cancel{\dot{Q}_{\mathrm{cv}}} - \dot{W}_{\mathrm{cv}} + \dot{m}\left[(h_1 - h_2) + \cancel{\frac{(\mathrm{V}_1^2 - \mathrm{V}_2^2)}{2}} + \cancel{g(z_1 - z_2)}\right]$$

- **If the change in kinetic energy of flowing matter is negligible, $\frac{1}{2}(\mathrm{V}_1^2 - \mathrm{V}_2^2)$ 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, $\dot{Q}_{\mathrm{cv}}$ drops out.**

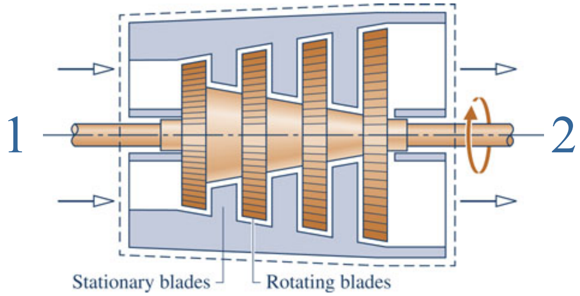
$$\frac{\dot{W}_{\mathrm{cv}}}{\dot{m}} = h_1 - h_2$$

where

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

Isentropic Turbine Efficiency

- For a turbine, the entropy rate balance reduces to



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

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

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