

3.7. Combining the First and Second Laws

Recall that for a system, the First Law of Thermodynamics, written on a per mass and differential basis, is,

$$de_{\text{sys}} = \delta q_{\text{into sys}} + \delta w_{\text{on sys}}. \quad (3.157)$$

If we consider a pure, simple, compressible substance (no kinetic or potential energies to consider and only pdV work), then Eq. (3.157) may be written as,

$$du = \delta q_{\text{into}} - pdv. \quad (3.158)$$

Note that the subscript “sys” has been dropped for convenience. Using the Second Law (Eq. (3.146)) to substitute for the heat transfer term and noting that when we use Eq. (3.146), we’re assuming an internally reversible process,

$$du = Tds - pdv \implies \boxed{Tds = du + pdv}, \quad (3.159)$$

or, if written in terms of the enthalpy ($dh = du + pdv + vdp$),

$$\boxed{Tds = dh - vdp} \quad (3.160)$$

Note that pdv work is considered internally reversible work if done quasi-statically. The boxed equations are known as the Tds equations and are useful in relating changes in entropy to other system properties.

Notes:

- (1) Even though the Tds equations were derived making use of an internally reversible process, since the equations only involve properties, the process used to go between the states is irrelevant. The Td equations hold for reversible and irreversible process paths.
- (2) Recall that during a change of phase, e.g., in the vapor dome, the pressure and temperature of a substance remain constant $\implies dp = 0$ and $T = \text{constant}$. Thus, Eq. (3.160) indicates that,

$$ds = \frac{dh}{T} \implies \Delta s = \frac{\Delta h}{T} \quad (\text{during a phase change}). \quad (3.161)$$

- (3) For an incompressible substance, $dv = 0$ and $du = c(T)dT$ so that Eq. (3.159) becomes,

$$Tds = c(T)dT \implies ds = c(T)\frac{dT}{T} \implies \boxed{s_2 - s_1 = \int_{T_1}^{T_2} \frac{c(T)}{T} dT} \quad (\text{incompressible substance}). \quad (3.162)$$

The change in specific entropy depends only on the (absolute) temperature. If we can further assume that c is constant (a reasonable assumption in many instances when the change in temperature is less than a few hundred Kelvin or degrees Rankine), then Eq. (3.162) becomes,

$$\boxed{s(T_2) - s(T_1) = c \ln\left(\frac{T_2}{T_1}\right)} \quad (\text{incompressible substance, constant specific heat}). \quad (3.163)$$

- (4) For an ideal gas, $pv = RT$ ($vdp + pdv = RdT$), $du = c_v(T)dT$, and $dh = c_p(T)dT$, so that Eq. (3.159) becomes,

$$Tds = c_v(T)dT + RdT - vdp = c_v(T)dT + RdT - RT\frac{dp}{p} = [c_v(T) + R]dT - RT\frac{dp}{p}. \quad (3.164)$$

Recall that for an ideal gas that $c_p(T) = c_v(T) + R$ so that the previous equation becomes,

$$ds = c_p(T)\frac{dT}{T} - R\frac{dp}{p}. \quad (3.165)$$

Integrating this equation gives,

$$\boxed{s(T_2, p_2) - s(T_1, p_1) = \int_{T_1}^{T_2} c_p(T)\frac{dT}{T} - R \ln\left(\frac{p_2}{p_1}\right)} \quad (\text{ideal gas}). \quad (3.166)$$

Similarly, Eq. (3.160) becomes,

$$Tds = dh - vdp = c_p(T)dT - RdT + pdv = [c_p(T) - R]dT + RT\frac{dv}{v}, \quad (3.167)$$

$$ds = c_v(T)\frac{dT}{T} + R\frac{dv}{v} = c_v(T)\frac{dT}{T} - R\frac{d\rho}{\rho}, \quad (3.168)$$

$$s(T_2, v_2) - s(T_1, v_1) = \int_1^2 \frac{c_v(T)}{T} dT + R \ln\left(\frac{dv}{v}\right) = \int_1^2 \frac{c_v(T)}{T} dT - R \ln\left(\frac{\rho_2}{\rho_1}\right) \quad (3.169)$$

Note that $\rho = 1/v \implies d\rho = -dv/v^2 \implies d\rho/\rho = -dv/v$ has been used in the previous equations. Since evaluating the integral involving $c_p(T)$ in Eq. (3.166) is inconvenient, let's define a new variable,

$$s^\circ(T) = \int_{T'}^T \frac{c_p(T)}{T} dT, \quad (3.170)$$

where T' is an arbitrary reference temperature. Values of $s^\circ(T)$ are frequently presented in thermodynamic tables for various ideal gases and on a per mole basis (e.g., Tables A-22 and A-23 in Moran et al., 8th ed.; refer to Figure 3.38). The integral involving $c_p(T)$ can now be written as,

$$s^\circ(T_2) - s^\circ(T_1) = \int_{T'}^{T_2} \frac{c_p(T)}{T} dT - \int_{T'}^{T_1} \frac{c_p(T)}{T} dT = \int_{T_1}^{T_2} \frac{c_p(T)}{T} dT, \quad (3.171)$$

and Eq. (3.166) may be written as,

$$s(T_2, p_2) - s(T_1, p_1) = s^\circ(T_2) - s^\circ(T_1) - R \ln\left(\frac{p_2}{p_1}\right) \quad (\text{ideal gas}). \quad (3.172)$$

TABLE A-22											
Ideal Gas Properties of Air											
T(K), h and u(kJ/kg), s° (kJ/kg · K)											
T	h	u	s°	when Δs = 0°		T	h	u	s°	when Δs = 0	
				p_r	v_r					p_r	v_r
200	199.97	142.56	1.29559	0.3363	1707.	450	451.80	322.62	2.11161	5.775	223.6
210	209.97	149.69	1.34444	0.3987	1512.	460	462.02	329.97	2.13407	6.245	211.4
220	219.97	156.82	1.39105	0.4690	1346.	470	472.24	337.32	2.15604	6.742	200.1
230	230.02	164.00	1.43557	0.5477	1205.	480	482.49	344.70	2.17760	7.268	189.5
240	240.02	171.13	1.47824	0.6355	1084.	490	492.74	352.08	2.19876	7.824	179.7

FIGURE 3.38. Ideal gas properties for air, including s° values. This table is from Moran et al., 8th ed.

- (5) If we assume we're dealing with a perfect gas (c_v and c_p are constants), Eqs. (3.166) and (3.169) become,

$$s(T_2, p_2) - s(T_1, p_1) = c_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{p_2}{p_1}\right) \quad (\text{perfect gas}) \quad (3.173)$$

$$s(T_2, v_2) - s(T_1, v_1) = c_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right) \quad (\text{perfect gas}) \quad (3.174)$$

$$s(T_2, \rho_2) - s(T_1, \rho_1) = c_v \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{\rho_2}{\rho_1}\right) \quad (\text{perfect gas}) \quad (3.175)$$

(6) For an isentropic process involving an ideal gas, Eq. (3.172) simplifies to,

$$0 = s^\circ(T_2) - s^\circ(T_1) - R \ln \left(\frac{p_2}{p_1} \right). \quad (3.176)$$

Re-arranging this equation gives,

$$\frac{p_2}{p_1} = \exp \left[\frac{s^\circ(T_2) - s^\circ(T_1)}{R} \right] = \frac{\exp \left[\frac{s^\circ(T_2)}{R} \right]}{\exp \left[\frac{s^\circ(T_1)}{R} \right]}. \quad (3.177)$$

For convenience, define a new parameter, p_r (note that this is not the reduced pressure used in determining the compressibility factor Z), so that Eq. (3.177) becomes,

$$p_r(T) := \exp \left[\frac{s^\circ(T)}{R} \right], \quad (3.178)$$

so that Eq. (3.177) becomes,

$$\frac{p_2}{p_1} = \frac{p_r(T_2)}{p_r(T_1)}. \quad (3.179)$$

The parameter $p_r(T)$ is often pre-tabulated as a function of temperature for common ideal gases, such as air (for example, refer to Table A-22 in Moran et al., 8th ed., shown in Figure 3.38). A similar approach can be used for determining the relationship between specific volume and temperature. Using the ideal gas law,

$$\frac{v_2}{v_1} = \frac{\frac{RT_2}{p_2}}{\frac{RT_1}{p_1}} = \frac{\frac{RT_2}{p_r(T_2)}}{\frac{RT_1}{p_r(T_1)}} = \frac{v_r(T_2)}{v_r(T_1)}, \quad (3.180)$$

where,

$$v_r(T) := \frac{RT}{p_r(T)}. \quad (3.181)$$

As with $p_r(T)$, $v_r(T)$ is often pre-tabulated for common ideal gases, such as air (refer to Table A-22 in Moran et al., 8th ed.; Figure 3.38). Using the quantities $p_r(T)$ and $v_r(T)$ in tabulated form makes it easier to perform calculations involving an ideal gas with variable specific heats. The influence of the variations of the specific heats with temperature are pre-calculated in the variables p_r and v_r .

(7) For an isentropic process involving a perfect gas, Eqs. (3.173) - (3.175) reduce to,

$$0 = c_p \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{p_2}{p_1} \right) \implies \frac{p_2}{p_1} = \left(\frac{T_2}{T_1} \right)^{\frac{c_p}{R}} = \left(\frac{T_2}{T_1} \right)^{\frac{c_p}{c_p - c_v}} = \left(\frac{T_2}{T_1} \right)^{\frac{c_p/c_v}{c_p/c_v - 1}}, \quad (3.182)$$

$$\boxed{\frac{p_2}{p_1} = \left(\frac{T_2}{T_1} \right)^{\frac{k}{k-1}}}, \quad (3.183)$$

$$0 = c_v \ln \left(\frac{T_2}{T_1} \right) + R \ln \left(\frac{v_2}{v_1} \right) \implies \frac{v_2}{v_1} = \left(\frac{T_2}{T_1} \right)^{\frac{-c_v}{R}} = \left(\frac{T_2}{T_1} \right)^{\frac{-c_v}{c_p - c_v}} = \left(\frac{T_2}{T_1} \right)^{\frac{1}{1 - c_p/c_v}}, \quad (3.184)$$

$$\boxed{\frac{v_2}{v_1} = \left(\frac{T_2}{T_1} \right)^{\frac{1}{1-k}}}, \quad (3.185)$$

$$0 = c_v \ln \left(\frac{T_2}{T_1} \right) - R \ln \left(\frac{\rho_2}{\rho_1} \right) \implies \frac{\rho_2}{\rho_1} = \left(\frac{T_2}{T_1} \right)^{\frac{c_v}{R}} = \left(\frac{T_2}{T_1} \right)^{\frac{c_v}{c_p - c_v}} = \left(\frac{T_2}{T_1} \right)^{\frac{1}{c_p/c_v - 1}}, \quad (3.186)$$

$$\boxed{\frac{\rho_2}{\rho_1} = \left(\frac{T_2}{T_1} \right)^{\frac{1}{k-1}}}. \quad (3.187)$$

Combining Eqs. (3.183) and (3.185) shows,

$$\boxed{\frac{p_2}{p_1} = \left(\frac{v_2}{v_1}\right)^{-k}} \implies p = \frac{c}{v^k} \implies pv^k = c, \quad (3.188)$$

where c is a constant. Hence, an isentropic process involving a perfect gas is a polytropic process with $n = k$, where n is the exponent in the polytropic process equation. Note that if $n = 1$ for an ideal gas, then the polytropic process is isothermal ($pv = RT$). If $n = 0$, then the process is isobaric (constant pressure). If $n = \pm\infty$, then the process is isometric (constant volume).

- (8) There are many engineering situations in which the isentropic assumption is a reasonable approximation to real life. For example, in high speed gas flows through nozzles and diffusers, the heat transfer is often small (\rightarrow adiabatic) and the irreversibilities due to viscous dissipation are concentrated in a thin boundary layer adjacent to the walls of the devices. Hence, most of the flow can be considered adiabatic and reversible, meaning that it can also be considered isentropic. This approximation is used frequently in high-speed gas flows. Since air is often the fluid of interest, we often make the additional assumption that the flow involves an ideal or perfect gas. Hence, the previous equations described in Notes 6 and 7 are frequently used.

A vendor claims that an adiabatic air compressor takes in air at standard atmospheric conditions and delivers the air at 650 kPa (gage) and 285 °C. Is this possible? Justify your answer.

SOLUTION:

Use the 2nd Law of Thermodynamics to determine whether or not the process can occur.

At the inlet (state 1), we have standard atmospheric conditions:

$$p_1 = 101 \text{ kPa}, T_1 = 293 \text{ K} \quad (1)$$

At the outlet (state 2):

$$p_2 = (650 + 101) \text{ kPa}, T_2 = (285 + 273) \text{ K} \quad (2)$$

The change in entropy between the states may be found using the following relation, which assumes that air behaves as a perfect gas:

$$s_2 - s_1 = c_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{p_2}{p_1}\right) \quad (3)$$

Substitute the given values:

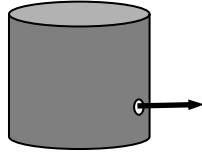
$$s_2 - s_1 = (1004 \text{ J}/(\text{kg} \cdot \text{K})) \ln\left(\frac{558 \text{ K}}{293 \text{ K}}\right) - (287 \text{ J}/(\text{kg} \cdot \text{K})) \ln\left(\frac{751 \text{ kPa}}{101 \text{ kPa}}\right) \quad (4)$$

$$\boxed{\therefore s_2 - s_1 = 71 \text{ J}/(\text{kg} \cdot \text{K})} \quad (5)$$

Since for an adiabatic process we must have $\Delta s \geq 0$, the process is feasible.

A rigid, insulated tank with a volume of 21.61 ft^3 is filled initially with air at 100 psia and $535 \text{ }^\circ\text{R}$. A leak develops and air slowly escapes until the pressure of the air remaining in the tank is 15 psia . Determine the mass of air remaining in the tank and its temperature.

SOLUTION:



Assume the leaking process is adiabatic because the tank is insulated, and reversible since the air is leaking slowly. Since the process is adiabatic and reversible, it's also isentropic. Furthermore, treat the air as an ideal gas. For an ideal gas undergoing an isentropic process,

$$\frac{p_2}{p_1} = \frac{p_r(T_2)}{p_r(T_1)} \Rightarrow p_r(T_2) = p_r(T_1) \left(\frac{p_2}{p_1} \right), \quad (1)$$

where $p_1 = 30 \text{ psia}$, $p_2 = 15 \text{ psia}$, and $p_r(T_1 = 535 \text{ }^\circ\text{R}) = 1.3423$ (interpolating in Table A-22E, Moran et al., 8th ed.),

$$\Rightarrow p_r(T_2) = 0.6711.$$

Interpolating in Table A-22E, we find that $T_2 = 439 \text{ }^\circ\text{R}$.

Note that if we assume air is a perfect gas (an ideal gas with constant specific heats), then for an isentropic process,

$$\frac{p_2}{p_1} = \left(\frac{T_2}{T_1} \right)^{\frac{k}{k-1}} \Rightarrow T_2 = T_1 \left(\frac{p_2}{p_1} \right)^{\frac{k-1}{k}}, \quad (2)$$

$\Rightarrow T_2 = 439 \text{ }^\circ\text{R}$, which is identical to the result found assuming ideal gas behavior.

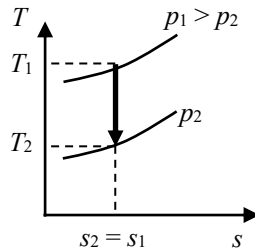
The mass of air remaining in the tank may be found using the ideal gas law,

$$p_2 V_2 = m_2 R T_2 \Rightarrow m_2 = (p_2 V_2) / (R T_2), \quad (3)$$

where $V_2 = 21.61 \text{ ft}^3$, $\bar{R}_u = 1545 \text{ ft}\cdot\text{lb}/(\text{lbmol}\cdot^\circ\text{R})$, and $M = 28.97 \text{ lb}_m/\text{lbmol}$,

$$\Rightarrow R_{\text{air}} = \bar{R}_u / M = (1545 \text{ ft}\cdot\text{lb}/(\text{lbmol}\cdot^\circ\text{R})) / 28.97 \text{ lb}_m/\text{lbmol} = 53.33 \text{ ft}\cdot\text{lb}/(\text{lb}_m\cdot^\circ\text{R}),$$

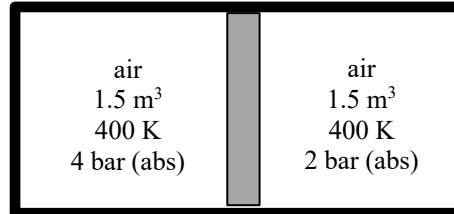
$$\Rightarrow m_2 = 1.99 \text{ lb}_m.$$



An insulated box is initially divided into halves by a frictionless, thermally conducting piston. On one side of the piston is 1.5 m^3 of air at 400 K , 4 bar (abs) . On the other side is 1.5 m^3 of air at 400 K , 2 bar (abs) . The piston is released and equilibrium is attained, with the piston experiencing no change of state.

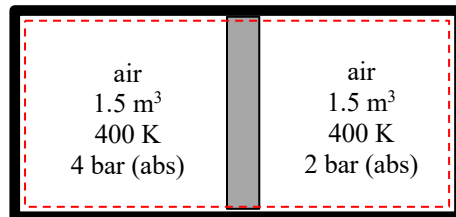
Determine:

- the final temperature,
- the final pressure, and
- the entropy produced.



SOLUTION:

Apply the 1st Law to a system consisting of the two chambers of air and the piston,



$$\Delta E_{\text{sys}} = Q_{\text{into sys}} + W_{\text{on sys}} \Rightarrow \Delta U_{\text{sys}} = 0 \quad (1)$$

where $\Delta E_{\text{sys}} = \Delta U_{\text{sys}}$ (no changes in kinetic and potential energies), $Q_{\text{into sys}} = 0$ (adiabatic) and $W_{\text{on sys}} = 0$ (rigid tank). Noting also that,

$$\Delta U_{\text{sys}} = \Delta U_1 + \Delta U_2 + \Delta U_{\text{piston}}, \quad (2)$$

where ΔU_1 is the change in the internal energy of the air on the left hand side, ΔU_2 is the change in internal energy of the air on the right hand side, and ΔU_{piston} is the change in internal energy of the piston ($\Delta U_{\text{piston}} = 0$), Eq. (2) may be written as,

$$\Delta U_1 + \Delta U_2 = 0 \Rightarrow m_1 \Delta u_1 + m_2 \Delta u_2 = 0 \Rightarrow m_1(u_{1,f} - u_{1,i}) + m_2(u_{2,f} - u_{2,i}) = 0. \quad (3)$$

Since the initial temperatures of the air are the same ($T_{1,i} = T_{2,i} = T_i = 400 \text{ K}$), $u_{1,i} = u_{2,i} = u_i$ (assuming air behaves as an ideal gas) and since at final equilibrium the temperatures are also the same ($T_{1,f} = T_{2,f} = T_f$), $u_{1,f} = u_{2,f} = u_f$,

$$\begin{aligned} (m_1 + m_2)u_f - (m_1 + m_2)u_i &= 0, \\ \Rightarrow u_f = u_i &\Rightarrow \boxed{T_f = T_i = 400 \text{ K}}. \end{aligned} \quad (4)$$

The final pressures in each chamber will also be equal at equilibrium,

$$p_{1,f} = p_{2,f} = p_f. \quad (5)$$

From the ideal gas law applied to the whole system,

$$p_f = \frac{(m_1 + m_2)RT_f}{(V_{1,f} + V_{2,f})}, \quad (6)$$

where $V_{1,f} + V_{2,f} = V_{1,i} + V_{2,i} = V_{\text{total}} = 3.0 \text{ m}^3$. The masses in each chamber may also be found using the ideal gas law and the initial conditions,

$$m_1 = \frac{p_{1,i} V_{1,i}}{RT_{1,i}} \quad \text{and} \quad m_2 = \frac{p_{1,i} V_{1,i}}{RT_{1,i}}. \quad (7)$$

where,

$$p_{1,i} = 4 \text{ bar} = 4 \cdot 10^5 \text{ Pa}$$

$$V_{1,i} = V_{2,i} = 1.5 \text{ m}^3$$

$$R_{\text{air}} = 287 \text{ J/(kg.K)}$$

$$T_{1,i} = T_{2,i} = 400 \text{ K}$$

$$p_{2,f} = 2 \text{ bar} = 2 \cdot 10^5 \text{ Pa}$$

$$\Rightarrow m_1 = 5.23 \text{ kg and } m_2 = 2.61 \text{ kg}$$

$$\Rightarrow \boxed{p_f = 3 \cdot 10^5 \text{ Pa} = 3 \text{ bar}}$$

The entropy produced during the process may be determined using the Tds equation for an ideal gas,

$$s_{1,f} - s_{1,i} = s^0(T_{1,f}) - s^0(T_{1,i}) - R \ln\left(\frac{p_{1,f}}{p_{1,i}}\right), \quad (8)$$

$$s_{2,f} - s_{2,i} = s^0(T_{2,f}) - s^0(T_{2,i}) - R \ln\left(\frac{p_{2,f}}{p_{2,i}}\right), \quad (9)$$

where, since $T_f = T_i$, the s^0 terms cancel. Using the given and calculated pressures,

$$s_{1,f} - s_{1,i} = 8.26 \cdot 10^1 \text{ J/(kg.K)},$$

$$s_{2,f} - s_{2,i} = -1.16 \cdot 10^2 \text{ J/(kg.K)}.$$

The total change in entropy for the system is,

$$S_f - S_i = m_1 \Delta s_1 + m_2 \Delta s_2, \quad (10)$$

$$\Rightarrow \boxed{\Delta S = 1.27 \cdot 10^2 \text{ kJ/K}}$$

