Chapter 1 THE FIRST LAW

Problem 1.1

 $W_{i-f} = \int_{i}^{f} P dV = P_1 V_2$. Next, to calculate T_f , we note that from state (a) (i) to state (f), we have

 $\frac{dM}{dt} = \dot{m}$ $\frac{dU}{dt} = -\dot{W} + \dot{m}h_1$

where m is the instantaneous flow rate into the cylinder and M and U are the mass and energy inventories of the system (the "system" is the cylinder volume). Integrating in time,

$$M_{f} - M_{i} = \int_{i}^{f} \dot{m} dt$$

$$U_{f} - U_{i} = -P_{1}V_{2} + h_{1}(M_{f} - M_{i}) \qquad (1)$$

and recognizing that $U_i = 0$ and $M_i = 0$, the first law reduces to $U_{f} = M_{f}h_{1} - P_{1}V_{2}$ (1')

For the "ideal gas" working fluid, we write

$$U_{f} = M_{f}c_{v}(T_{f} - T_{0})$$

 $h_{1} = c_{v}(T_{1} - T_{0}) + Pv_{1}$

hence, eq. (1') becomes

 $M_f c_v (T - T_0) = M_f [c_v (T_1 - T_0) + Pv_1] - P_1 V_2$

Noting that $V_2 = M_f V_f$ and dividing everything by M_f yields

$$c_v T_f + P_1 v_f = c_v T_1 + P v_f$$

or

 $c_{v}T_{f} + RT_{f} = c_{v}T_{1} + RT_{1}$

in other words, $T_f = T_1$. The final ideal-gas mass admitted is $\mathbf{m}_{\mathrm{f}} = \mathbf{M}_{\mathrm{f}} = \frac{\mathbf{P}_{\mathrm{I}}\mathbf{V}_{\mathrm{2}}}{\mathbf{R}\mathbf{T}_{\mathrm{f}}}$

hence the goodness ratio

$$\frac{W_{i-f}}{m_f} = \frac{P_1 V_2}{P_1 V_2 / (R T_1)} = R T_1$$

(b) $m_1 = P_1 V_1 / R T_1$, based on the solution for mf given in part (a), and
 $W_{i-f} = \int_0^{V_1} P dV + \int_{V_1}^{V_2} P dV$
 $= P_1 V_1 + \frac{c_v}{R} (P_1 V_1 - P_2 V_2)$

The second group of terms on the right-hand side is the work output during the reversible and adiabatic expansion (path: $PV^k = constant$). Finally, the goodness ratio is

$$\frac{W_{i-f}}{m_1} = \frac{P_1 V_1 + \frac{c_v}{R} (P_1 V_1 - P_2 V_2)}{P_1 V_1 / (R T_1)} = R T_1 \left[1 + \frac{c_v}{R} \left(1 - \frac{P_2 V_2}{P_1 V_1} \right) \right]$$

(c) The relative goodness is

$$\frac{(W_{i-f}/m_1)_{part(b)}}{(W_{i-f}/m_f)_{part(a)}} = 1 + \frac{c_v}{R} \left(1 - \frac{P_2 V_2}{P_1 V_1} \right)$$
$$= 1 + \frac{c_v}{R} \left(1 - \left(\frac{V_1}{V_2} \right)^{k-1} \right)$$

The quantity in the square brackets is positive because k > 1 and $V_1 < V_2$; therefore,

$$\left(\frac{\mathbf{W}_{i-f}}{\mathbf{m}_{1}}\right)_{\text{part(b)}} > \left(\frac{\mathbf{W}_{i-f}}{\mathbf{m}_{f}}\right)_{\text{part(a)}}$$

Problem 1.2

(a) Given are m = 1 kg, $T_1 = 100^{\circ}\text{C}$, and $x_1 = 0.5$. The path is constant volume.



(b) To pinpoint state (2), we must determine two properties at the final state. The first one is the volume

$$v_2 = v_1 = v_{f,T_1} + x_1 v_{fg,T_1} =$$

= 0.001044 + 0.5(1.6729 - 0.001044)
= 0.837 m³ / kg

The second property is the internal energy: this comes from the first law

$$Q_{1-2} - W_{1-2} = m(u_2 - u_1)$$
 (1)
where $W_{1-2} = 0$ and
 $u_1 = u_{f,T_1} + x_1 u_{fg,T_1} = 418.94 + (0.5)(2087.6) = 1462.74 \text{ kJ/kg}$
Equation (1) yields

$$u_2 = u_1 + \frac{1}{m}Q_{1-2} = 3662 \text{ kJ/kg}$$

(c) To find T_2 and P_2 , we must first locate state (2) on the P(v, t) surface (or tables). At state (2), we know u_2 and v_2 ; therefore, one way to proceed is to look at the table of superheated steam properties and find the u values of order 3662 kJ/kg. This is the equivalent of traveling along the $u = u_2$ line and looking for the v value that comes closest to v_2 This search leads to this portion of the table:

Т	P = 0.5 MPa		P = 0.6 MPa	
	V	u	V	u
	•••			•••
800°C	0.9896	3662.1	0.8245	3661.8
•••	•••	•••	••••	•••

Fitting v_2 between 0.9896 and 0.8245, we interpolate linearly for pressure and find

$$P_2 \cong 0.592 \text{ MPa}$$

The final temperature is $T_2 \cong 800^{\circ}$ C.

- (d) At state (2), the system is superheated steam. This particular fluid approaches ideal gas behavior if near state (2) the following *two conditions* are met:
 - (i) u = u(T)
 - (ii) Pv = RT, i.e., Pv / T = constant

Condition (i) is satisfied, as shown by the u values listed in the preceding table. (u depends on T, while being practically independent of P.) As a way of testing condition (ii), we calculate the group (Pv/T) for the states immediately to the left and right of state (2):

$$\left(\frac{Pv}{T}\right)_{left} = \frac{(0.5)10^{6}(0.9896)}{273.15+800} = 461.1\frac{Pa \text{ m}^{3}/\text{kg}}{\text{K}}$$
$$\left(\frac{Pv}{T}\right)_{right} = \frac{(0.5)10^{6}(0.8245)}{273.15+800} = 461.0\frac{Pa \text{ m}^{3}/\text{kg}}{\text{K}}$$

Condition (ii) is also satisfied (approximately, of course); therefore, the ideal gas model could be used to describe the behavior of the system at states that are sufficiently close to state (2).

Observation: Note the use of absolute temperature in the denominators of the (Pv/T) calculations presented above.

Problem 1.3

Taking the m gas as "system," we write the first law for the process (1) - (2),

$$Q_{1-2} - W_{1-2} = U_2 - U_1$$

which means

$$0 - P_{1A}(V_2 - V_1) = \frac{m}{3}c_v(T_2 - T_1) + \frac{m}{3}c_v(T_2 - T_1) + \frac{m}{3}c_v(T_2 - T_1)$$

or

$$-P_{1A}\left(\frac{mRT_{2}}{P_{2}} - \frac{\frac{m}{3}RT_{1}}{P_{1A}} - \frac{\frac{m}{3}RT_{1}}{P_{1B}} - \frac{\frac{m}{3}RT_{1}}{P_{1C}}\right) = mc_{v}(T_{2} - T_{1})$$

Noting that $P_2 = P_{1A}$, the above statement can be written as

$$\frac{T_2}{T_1} = \frac{1}{1 + R/c_v} + \frac{1 + (P_{1A} / P_{1B}) + (P_{1A} / P_{1C})}{3(1 + R/c_v)} \cdot \frac{R}{c_v}$$
$$= \frac{c_v}{c_p} + \frac{R}{3c_p} \left(1 + \frac{P_{1A}}{P_{1B}} + \frac{P_{1A}}{P_{1C}}\right)$$

Problem 1.4

The process is one of heating at constant volume. Let m_f and m_g represent the instantaneous liquid and vapor inventories in the system,

$$m_f + m_g = m$$
, (constant) (1)

Furthermore, the constant-volume constraint reads

$$m_f v_f + m_g v_g = V$$
, (constant) (2)

The first law of thermodynamics requires on a per-unit-time basis that

$$\dot{\mathbf{Q}} - \dot{\mathbf{W}} = \frac{\mathrm{d}\mathbf{U}}{\mathrm{d}t}$$

or, since $\dot{W} = 0$,

$$\dot{Q} = \frac{d}{dt} (m_{f}u_{f} + m_{g}u_{g})$$

$$= u_{f} \frac{dm_{f}}{dt} + m_{f} \frac{du_{f}}{dt} + u_{g} \frac{dm_{g}}{dt} + m_{g} \frac{du_{g}}{dt}$$

$$\frac{du_{g}}{dt} \frac{du_{g}}{dt} \frac{du_{g}}{dt} \frac{du_{g}}{dt}$$
(3)

The time derivatives dm_f/dt and dm_g/dt follow from solving the system of two equations

$$\frac{d}{dt}$$
 (1) and $\frac{d}{dt}$ (2)

The solution is

$$\frac{\mathrm{dm}_{\mathrm{f}}}{\mathrm{dt}} = -\frac{\mathrm{A}}{\mathrm{v}_{\mathrm{fg}}} \quad \text{and} \quad \frac{\mathrm{dm}_{\mathrm{g}}}{\mathrm{dt}} = -\frac{\mathrm{A}}{\mathrm{v}_{\mathrm{fg}}} \tag{4}$$

where

$$A = -m_{f} \frac{dv_{f}}{dt} - m_{g} \frac{dv_{g}}{dt} = -m_{f} \frac{dv_{f}}{dP} \frac{dP}{dt} - m_{g} \frac{dv_{g}}{dP} \frac{dP}{dt}$$

Combining Eqs. (3) and (4), we obtain after a few manipulations

$$\frac{\mathrm{dP}}{\mathrm{dt}} = \frac{\dot{Q}/m}{\frac{\mathrm{du}_{\mathrm{f}}}{\mathrm{dP}} - \frac{\mathrm{u}_{\mathrm{fg}}}{\mathrm{v}_{\mathrm{fg}}}} \frac{\mathrm{dv}_{\mathrm{f}}}{\mathrm{dP}} + x \left(\frac{\mathrm{du}_{\mathrm{fg}}}{\mathrm{dP}} - \frac{\mathrm{u}_{\mathrm{fg}}}{\mathrm{v}_{\mathrm{fg}}}}{\frac{\mathrm{dv}_{\mathrm{fg}}}{\mathrm{dP}}}\right)$$

Problem 1.5

Applying the first law to the water containers as an open system, we have (a) $\frac{\mathrm{d}}{\mathrm{dt}}(\mathrm{mu}) = (\dot{\mathrm{m}}\mathrm{h})_{\mathrm{in}} - (\dot{\mathrm{m}}\mathrm{h})_{\mathrm{out}}$ (1)where V $m = \frac{V}{v} = constant$ T(t) Mass conservation dictates $\frac{\mathrm{d}}{\mathrm{dt}}(\mathrm{m}) = \dot{\mathrm{m}}_{\mathrm{in}} - \dot{\mathrm{m}}_{\mathrm{out}} = 0$ hence $\dot{m}_{in} = \dot{m}_{out} = \dot{m}$. The first law (1) reads finally $\frac{V}{V_{w}}\frac{du}{dt} = \dot{m}(h_{in} - h_{out})$ For an incompressible fluid we also have du = cdT and $dh = cdT + v_w dP$ In the present case, $P_{in} = P_{out}$; therefore, $h_{in} - h_{out} = c(T_{in} - T_{out}) = c(T_2 - T)$ Equation (1) becomes $\frac{V}{v_{m}}c\frac{dT}{dt} = \dot{m}c(T_2 - T)$ which, integrated from 0 to t, means $\ln\frac{T_2-T}{T_2-T_1} = -\frac{\dot{m}v_w}{V}t$ (b) The mass of hot water that raises the container water temperature from 10°C to 20°C is $\dot{m}t = -\frac{V}{V_{w}} \ln \frac{T_2 - T_1}{T_2 - T_1}$ $= -\frac{\mathrm{m}^{3}}{10^{-3} \mathrm{m}^{3} / \mathrm{kg}} \ln \frac{40 - 20}{40 - 10} = 405.5 \mathrm{kg}$

Problem 1.6

Selected for analysis is the system that contains the two masses (m_1, m_2) . In the initial state (a), the velocities of the two masses are different (V_1, V_2) , while in the final state (b), mutual friction brings the velocities to the same level (V_{∞}) . Since there are no forces between the system and its environment, the total momentum of the ensemble is conserved,

$$m_1 V_1 + m_2 V_2 = (m_1 + m_2) V_{\infty}$$
⁽¹⁾

The initial and final kinetic energy inventories of the ensemble are

$$KE_{a} = \frac{1}{2}m_{1}V_{1}^{2} + \frac{1}{2}m_{2}V_{2}^{2}$$

$$KE_{b} = \frac{1}{2}(m_{1} + m_{2})V_{\infty}^{2}$$
(2)
(3)

The evolution of the total kinetic energy during the process (a)–(b) is described by the "efficiency" ratio

$$\eta = \frac{KE_t}{KE_a} \tag{4}$$

Eliminating V_{∞} between Eqs. (1) and (3), the efficiency can be expressed in terms of the initial mass and velocity ratios m_2/m_1 and V_2/V_1 ,

$$\eta = \frac{\left(1 + \frac{m_2}{m_1} \frac{V_2}{V_1}\right)^2}{\left(1 + \frac{m_2}{m_1}\right) \left[1 + \frac{m_2}{m_1} \left(\frac{V_2}{V_1}\right)^2\right]} < 1$$
(5)

It can be shown analytically that η is less than 1 as soon as V₂ is different from V₁, for any value of the ratio m_2/m_1 . Two limits of eq. (5) are worth noting:

$$\eta = \frac{1}{\frac{m_2}{m_1} + 1} \quad \left(\frac{V_2}{V_1} \to 0\right)$$

$$\eta = \frac{1}{\frac{m_1}{m_2} + 1} \quad \left(\frac{V_2}{V_1} \to \infty\right)$$
(6)
(7)

with the special case $\eta = 1$ when $V_1 = V_2$ for any m_2/m_1 . Equations (5)–(7) show that the order of magnitude of η is 1 when m_2/m_1 is a number of order 1.

In conclusion, the kinetic energy of the system decreases from state (a) to state (b). According to the first law of thermodynamics, this decrease is balanced by the other energy interactions and energy changes of the system,

$$Q_{a-b} - W_{a-b} = U_b - U_a + KE_b - KE_a$$
 (8)

where $W_{a-b} = 0$. If the process is adiabatic, $Q_{a-b} = 0$, then the KE decrease is balanced by an increase in U,

$$\mathbf{U}_{\mathrm{b}} - \mathbf{U}_{\mathrm{a}} = \mathbf{K}\mathbf{E}_{\mathrm{a}} - \mathbf{K}\mathbf{E}_{\mathrm{b}} \tag{9}$$

If the system boundary is diathermal, and (a) and (b) are states of thermal equilibrium with the ambient temperature reservoir (T_0) , then

$$Q_{a-b} = U_b - U_a + KE_b - KE_a$$
 (10)

If m_1 and m_2 are two incompressible substances, then U = U(T), and at thermal equilibrium (T₀), the energy change $U_b - U_a$ is zero, and

$$Q_{a-b} = KE_b - KE_a < 0 \tag{11}$$

Problem 1.7

The first law for a complete cycle is $\oint \delta Q - \oint \delta W = \oint dE = 0$

a) No, since $\oint \delta W = \oint \delta Q = 0$

b) No, since
$$\oint \delta Q = \oint \delta W = 0$$

- c) If the cycle has no net work transfer, then $\oint \delta Q = 0$. Processes that make up this cycle may have heat transfer interactions which, over the entire cycle, add up to zero.
- d) With no net heat transfer, there is no net work transfer for the cycle. Parts of the cycle, however, may have work transfer interactions that in the end cancel each other, $\oint \delta Q = 0$.

Problem 1.9

The system is closed (m, fixed), and the boundary is adiabatic. State 1 is pinpointed by V_1 and T_1 . At state 2, we know $V_2 = V_1$ (rigid enclosure). The temperature T_2 is determined by invoking the first law,

 $Q_{12} + W_{12} = U_2 - U_1$

where

 $W_{12} >0$, directed into the system $Q_{12} = 0$, adiabatic $U_{2}-U_{1} = m c (T_{2}-T_{1})$, incompressible substance

In conclusion,

$$\mathbf{T}_2 = \mathbf{T}_1 + \frac{\mathbf{W}_{12}}{\mathbf{m} \mathbf{c}}$$

Problem 1.10

The system is closed, the process 1-2 is at constant temperature, T, and the volume change is quasistatic, $\delta W = PdV$. If the system contains an ideal gas with initial volume V₁, from the first law, we have

$$\delta Q - \delta W = dU$$

$$\delta Q - PdV = m \text{ cv } dT \quad (dT = 0)$$

$$\delta Q = PdV = \delta W$$

$$Q12 = \int_{1}^{2} PdV = \int_{1}^{2} \frac{m R T}{V} dV$$

$$= m R T \ln \frac{V_{2}}{V_{1}} = W_{12}$$

Because dT = 0, we note that $U_2 - U_1 = 0$. In conclusion, for the ideal gas:

 $Q_{12} = W_{12}$ and $U_2 - U_1 = 0$

If the system contains initially saturated liquid (1 = f), the isothermal expansion is also an isobaric expansion. The first law yields

$$\begin{aligned} \mathbf{Q}_{12} &- \mathbf{W}_{12} = \mathbf{U}_2 - \mathbf{U}_1 \\ \mathbf{Q}_{12} &= \mathbf{W}_{12} + \mathbf{U}_2 - \mathbf{U}_1 \\ \mathbf{Q}_{12} &= \mathbf{W}_{12} + \mathbf{U}_2 - \mathbf{U}_1 \\ \mathbf{Q}_{12} &= \mathbf{P}_{1,2} (\mathbf{V}_2 - \mathbf{V}_1) + \mathbf{U}_2 - \mathbf{U}_1 \\ &= \mathbf{H}_2 - \mathbf{H}_1, \text{ or } \mathbf{H}_g - \mathbf{H}_f = \mathbf{m} \mathbf{h}_{fg} \end{aligned}$$

In conclusion, for the complete evaporation of the liquid (2 = g), the following results hold:

 $Q_{12} = m h_{fg}, \quad W_{12} = P m v_{fg}, \quad U_2 - U_1 = m u_{fg}$

Unlike in the ideal gas case, W_{12} is not the same as Q_{12} because the substance evaporating at constant temperature has the ability to store internal energy.

Problem 1.11

The relation between the temperature expressed in degrees °C and °F is

$$T(^{\circ}C) = \frac{5}{9} \left[\theta(^{\circ}F) - 32 \right]$$

The captain was correct if T and θ have the same numerical value, $T = \theta = x$. Substitute in the above relation we find that x = -40. The captain was correct.

Problem 1.12

The cavern is an open thermodynamic system with mass m(t) and energy E(t). The conservation of mass and energy require

$$\frac{\mathrm{dm}}{\mathrm{dt}} = \dot{\mathrm{m}}, \quad \mathrm{constant} \frac{\mathrm{dU}}{\mathrm{dt}} = \dot{\mathrm{mh}}_0 \qquad (1, 2)$$

where h_0 is constant. After combining (1) and (2),

 $\frac{dU}{dt} = \frac{d}{dt}(\dot{m}h_0)$ (3) $U = mh_0 + constant$ (4) $mu = mh_0 + constant$ (5)

where h_0 is the specific enthalpy of the air stream that enters the cavity. Initially, at t = 0, the pressure and temperature of the cavern are the same as those of the inflowing stream. These initial conditions are indicated by the subscript 0, therefore eq. (5) states that at t = 0

$$m_0 U_0 = m_0 h_0 + constant$$
 (6)

Eliminating the constant between Eqs. (5) and (6) and noting that eq. (1) yields equation, we obtain

 $mu - m_0 u_0 = \dot{m} th_0$ (6)

furthermore, because $m = m_0 + \dot{m}t$, $u - u_0 = c_v(T - T_0)$, $h_0 = u_0 P_0 v_0$, and $P_0 v_0 = R T_0$, eq. (6) becomes

$$\frac{\mathrm{T}}{\mathrm{T}_{0}} = 1 + \frac{\mathrm{R}}{\mathrm{c}_{\mathrm{v}}} \frac{\mathrm{\dot{m}t}}{\mathrm{m}_{0} + \mathrm{\dot{m}t}} \quad (7)$$

This shows that the cavern temperature T rises from T_0 to $(c_P/c_v)T_0$ during a time of order equation. This is the highest temperature rise during the filling of the cavern, because the cavern was modeled as adiabatic. If the cavern loses heat to its walls, then the final cavern temperature will be lower than $(c_P/c_v)T_0$.

Chapter 2 THE SECOND LAW

Problem 2.1

With reference to system A sketched below, assume that

W > 0 and $Q_2 > 0$

The first law for one cycle completed by A is

 $\mathbf{Q}_1 + \mathbf{Q}_2 = \mathbf{W} \quad (1)$

Investigating the possible signs of Q_1 and Q_2 , we see three options:

- (i) $Q_1 < 0 \text{ and } Q_2 < 0$
- (ii) $Q_1 > 0$ and $Q_2 > 0$
- (iii) $Q_1Q_2 < 0$

Option (i) is ruled out by the first law (1) and the assumption that W is positive. Option (ii) is a violation of the Kelvin-Planck statement (2.2). In order to see this violation, consider system B, which executes one complete cycle while communicating with (T_1) such that

 $Q_{\rm B} = -Q_1$

Since the net heat transfer interaction experienced by (T_1) is zero, $Q_1 + Q_B = 0$, the (T_1) reservoir completes a cycle at the end of the cycles executed by A and B. The aggregate system $[A + B + (T_1)]$ also executes a complete cycle. This cycle is executed while making contact with (T_2) only. The net heat transfer interaction of this cycle is positive

 $Q_2 > 0$

which is a clear violation of eq. (2.2). In conclusion, the only option possible is (iii): $Q_1Q_2 < 0$.



Problem 2.2

With reference to the system A shown in the preceding figure, we write the first law for one cycle

 $Q_1 + Q_2 = W$

(1)

and assume this time that W is negative,

W < 0

There are three options to consider:

(i) $Q_1 < 0 \text{ and } Q_2 < 0$ (ii) $Q_1 > 0 \text{ and } Q_2 > 0$ (iii) $Q_1Q_2 < 0$

of which only option (ii) can be ruled out, because it violates the first law. Option (i) is definitely compatible with the sign of eq. (2.27),

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} < 0$$
 (2.27)

Option (iii), in which Q_2 is the negative of the two heat transfer interactions, produces an analysis identical to the segment contained between eqs. (2.11) and (2.27) in the text. The second law (2.27) is valid therefore for W < 0 and as shown in the text for W > 0.

In the special case of W = 0, the first law requires that $Q_1 = -Q_2$. The second law (2.27) reduces to

 $Q_1(T_1 - T_2) > 0$

which means that

- (a) if Q_1 is positive, then $(T_1 T_2)$ cannot be negative, or
- (b) if Q_1 is negative, then $(T_1 T_2)$ cannot be positive.

In less abstract terms, (a) and (b) mean that in the absence of work transfer, the heat transfer interaction Q_1 cannot proceed in the direction of higher temperatures.

Problem 2.3

According to the problem statement, it is being assumed that *two* paths $(1 - 2_{rev})$ and $1 - 2'_{rev}$ can be traveled in both directions (see sketch below). The two paths are reversible and adiabatic. This assumption allows us to execute the cycle $1 - 2'_{rev} - 2_{rev} - 1$ in two ways:

(i) clockwise, in which

$$\oint \delta Q = Q_{2'_{rev}-2_{rev}} = U_{2_{rev}} - U_{2'_{rev}} > 0$$

(ii) counterclockwise, in which

$$\oint \delta Q = Q_{2_{rev}-2'_{rev}} = U_{2'_{rev}} - U_{2_{rev}} > 0$$

Note, however, that the counterclockwise option violates the Kelvin-Planck statement of the second law. This means that the original assumption on which options (i) and (ii) are based is false (i.e., that two reversible and adiabatic paths cannot intersect at state 1).

Is state 2_{rev} unique on the V = V₂ line? Worth noting is that options (i) and (ii) are both compatible with the Kelvin-Planck statement in the case where state $2'_{rev}$ (or, for the matter, any other state $2'_{rev}$ on the V = V₂ line) coincides with state 2_{rev} . In this case, the reading of the cycle goes as follows:

(i) clockwise

$$\oint \delta Q = Q_{2'_{rev}-2_{rev}} = 0$$
(ii) counterclockwise

$$\oint \delta \mathbf{Q} = \mathbf{Q}_{2_{\text{rev}} - 2'_{\text{rev}}} = \mathbf{0}$$

Geometrically, this second law compatible limit means that state 2_{rev} is unique (i.e., there is only one state at $V = V_2$ that can be reached reversibly and adiabatically from state 1).



Problem 2.4

(a) With reference to the sketch below, assume first that state 2 is such that

 $U_2 < U_{2_{rev}}$

Assume further that state 2 is accessible adiabatically from state 1. Then if we execute the cycle $1 - 2 - 2_{rev} - 1$ clockwise, we conclude that

$$\oint Q = Q_{2-2_{rev}} = U_{2_{rev}} = U_{2_{rev}} - U_{2} > 0$$

which is a violation of the Kelvin-Planck statement.

(b) Consequently we assume that the state 2' that is accessible adiabatically from state 1 is situated above state 2_{rev},

$$U_{2'} < U_{2_{rev}}$$

Executing the cycle $1 - 2' - 2_{rev} - 1$ counterclockwise, we conclude that

$$\oint \delta Q = Q_{2'-2_{rev}} = U_{2_{rev}} - U_{2'} < 0$$

which is in accord with the Kelvin-Planck statement.

In conclusion, the states that are accessible adiabatically from state 1 are all situated *above* state 2_{rev} . This conclusion is the same as the one reached in the discussion of Fig. 2.10 in the text.



Problem 2.5

Starting with state A, Fig. 2.8, we remove a *single* partition. We have three choices. Labeling the partitions (a), (b), and (c), we analyze each choice and list the results in line with each graph. For example, removing (a) allows the contents of the two leftmost chambers to mix to the new temperature $\frac{3}{2}$ T₀, which is listed on the drawing. The new entropy inventory of the aggregate system is in this case

$$\frac{S - S_0}{mc} = 2 \ln \frac{3}{2} + \ln 3 + \ln 4 = 3.296$$

This number is listed to the right of each drawing and represents the abscissa values of the points drawn in line with "2 partitions present" in Fig. 2.8.



Starting again from state A (3 partitions present), we remove *two* partitions at a time. We have the following choices and results:



Regarding the number of paths from A to B, we can have the following scenarios:

- (i) Removing a *single* partition each time, we have $3 \times 2 = 6$ choices, therefore 6 possible paths.
- (ii) Removing a *single* partition in the first step and *two* partitions in the second, we have $3 \times 1 = 3$ choices, meaning 3 paths.
- (iii) Removing *two* partitions in the first step and a *single* partition in the second, we have again $3 \times 1 = 3$ choices, hence 3 paths.
- (iv) Removing all three partitions at the same time, one path.

The total number of paths is then 6 + 3 + 3 + 1 = 13.

Problem 2.6

Assume first that the end state is (b), in other words, that the piston is pressed against the ceiling of the enclosures. The first law for the (gas + weight) system during the process (a) \rightarrow (b) is

$$Q_{a-b} - W_{a-b} = (U_b - U_a)_{gas} + (PE_b - PE_a)_{weight}$$
$$0 \quad 0 \quad mc_v (T_2 - T_1) \quad \frac{Mg}{A} (V_2 - V_1)$$

This equation delivers the final temperature,

$$T_{2} = T_{1} - \frac{Mg/A}{mc_{v}} (V_{2} - V_{1})$$
(1)

For configuration (b) to exist, the final pressure P_2 must be greater than the pressure that could be sustained by the piston weight alone,

$$P_2 > \frac{Mg}{A}$$

hence

$$\frac{\mathrm{mRT}_{2}}{\mathrm{V}_{2}} > \frac{\mathrm{Mg}}{\mathrm{A}}$$
(2)

Combining eqs. (2) and (1), this criterion becomes

$$\frac{1}{\frac{c_{\rm p}}{c_{\rm v}}} \frac{V_2}{V_1} - \frac{R}{c_{\rm v}} > \frac{Mg/A}{P_1}$$
(3)

The entropy generated during the process $(a) \rightarrow (b)$ is

$$S_{\text{gen,a-b}} = \left(S_{\text{b}} - S_{\text{a}}\right)_{\text{gas}} + \underbrace{\left(S_{\text{b}} - S_{\text{a}}\right)_{\text{weight}}}_{0} - \int_{\text{a}}^{\text{b}} \frac{\delta Q}{T}$$

$$= mc_{\text{v}} \ln \frac{T_{2}}{T_{1}} + mR \ln \frac{V_{2}}{V_{1}}$$
(4)

Using eq. (1), we can put eq. (4) in the following dimensionless form

$$\frac{\mathbf{S}_{\text{gen,a-b}}}{\mathbf{mc}_{v}} = \ln\left\{\left[1 - \frac{\mathbf{Mg/A}}{\mathbf{P}_{1}} \frac{\mathbf{R}}{\mathbf{c}_{v}} \left(\frac{\mathbf{V}_{2}}{\mathbf{V}_{1}} - 1\right)\right] \left(\frac{\mathbf{V}_{2}}{\mathbf{V}_{1}}\right)^{\mathbf{R/c}_{v}}\right\}$$
(5)

The objective is to show that the quantity calculated with eq. (5) is positive (i.e., that the quantity between accolades $\{ \}$ is greater than 1). The proof that $\{ \} > 1$ is

even stronger if we replace the factor $(Mg/A)P_1$ by its ceiling value, which is listed on the left side of the inequality (3). In other words, if we prove that

$$1 - \frac{\frac{R}{c_v} \left(\frac{V_2}{V_1} - 1\right)}{\frac{c_p}{c_v} \frac{V_2}{V_1} - 1} \left[\left(\frac{V_2}{V_1}\right)^{R/c_v} > 1 \right]$$
(6)

then we can be sure that S_{gen} , a-b of eq. (5) is positive. To prove the inequality (6) means to prove that

$$\frac{\left(\frac{\mathbf{V}_2}{\mathbf{V}_1}\right)^{\mathbf{R}/\mathbf{c}_v}}{\mathbf{R}/\mathbf{c}_v} > \frac{\frac{\mathbf{V}_2}{\mathbf{V}_1} - 1}{\frac{\mathbf{V}_2}{\mathbf{V}_1}}$$
(7)

Both sides of the inequality (7) are monotonic in (V_2 / V_1) . The inequality is clearly correct in the limit $V_2/V_1 \rightarrow \infty$. To see its true sign in the opposite limit, $V_2/V_1 \rightarrow 1$, let

$$\frac{V_2}{V_1} = 1 + \varepsilon$$
, where $\varepsilon << 1$

and rewrite eq. (7) side by side as

$$\varepsilon + \left(\frac{\mathbf{R}}{\mathbf{c}_{v}} - 1\right) \frac{\varepsilon^{2}}{2} \dots > \varepsilon - \varepsilon^{2} + \dots$$

This form reduces to

$$\frac{c_p}{c_v}\frac{\varepsilon^2}{2} > 0$$

which certainly validates eq. (7) in the limit $\varepsilon \to 0$. The inequality (7) is true for *all* values of V₂/V₁ in the range (1, ∞) because the derivative of the left side of eq. (7) with respect to (V₂/V₁) is always greater than the derivative of the right side,

$$\left(\frac{\mathbf{V}_2}{\mathbf{V}_1}\right)^{\frac{\mathbf{R}}{\mathbf{c}_v}-1} > \left(\frac{\mathbf{V}_2}{\mathbf{V}_1}\right)$$

for $(V_2/V_1) > 1$ and $(R/c_v) > 0$.

Consider next the process (a) \rightarrow (c), which occurs when eq. (3) is violated. The first law (1) for this case reads

$$T_3 = T_1 - \frac{Mg/A}{mc_v} (V_3 - V_1)$$

In order to find V_3 , we combine (3) with $P_3V_3 = mRT_3$; the result is

$$\frac{\mathbf{V}_3}{\mathbf{V}_1} = \frac{\mathbf{c}_{\mathrm{V}}}{\mathbf{c}_{\mathrm{P}}} \left(\frac{\mathbf{P}_1}{\mathbf{P}_3} + \frac{\mathbf{R}}{\mathbf{c}_{\mathrm{V}}} \right)$$

where $P_3 = Mg/A$. This result makes it easy to verify that when $P_1 = P_3$ the piston does not move at all, $V_3 = V_1$. Finally, the entropy generated during the process (a) \rightarrow (c) is

$$\frac{S_{\text{gen,a-c}}}{mc_{v}} = \ln \frac{T_{3}}{T_{1}} + \frac{R}{c_{v}} \ln \frac{V_{3}}{V_{1}}$$
$$= \ln \left[1 + \frac{1 - x}{\frac{c_{p}}{R} x - 1}\right] x^{R/c_{v}}$$

where x is shorthand for V_2/V_1 . To prove that the entropy increases from (a) to (c), we must prove

$$\left(1 + \frac{1 - x}{\frac{c_p}{R}x - 1}\right) x^{R/c_v} > 1$$

in other words:

$$\frac{\mathbf{x}^{\mathbf{k}} - 1}{\mathbf{k}} > \mathbf{x} - 1 \tag{10}$$

where $k = c_P/c_V$. Both sides of the inequality (10) approach zero in the limit $x \rightarrow 1$. In the opposite limit $(x \rightarrow \infty)$, the inequality is correct. It is correct also at intermediate x's, because the same inequality exists between the d()/dx slopes of the left and right sides of eq. (10), respectively.

$$x^{k-1} > 1,$$
 $\frac{d}{dx}$ [eq. (10)]

for x > 1 and k > 1.

Problem 2.7

The initial pressures above and below the partition are

$$P_{1 \text{ above}} = P_2 = \frac{Mg}{A}$$
, and $P_{1 \text{ below}} = \frac{mRT_1}{2V_1}$

The first law for the (m + M) system requires

$$Q_{a-b} - W_{a-b} = (U_b - U_a)_{gas} + (PE_b - PE_a)_{weight}$$

$$0 \qquad 0 \qquad mc_{v}(T_{2}-T_{1}) \qquad \frac{Mg}{A}(V_{b}-V_{a})$$

where

$$V_{b} = \frac{mRT_{2}}{R_{2}}$$

and

$$V_{a} = V_{1} + \frac{(m/2)RT_{1}}{Mg/A}$$

Combining these results, we obtain the expression for T_2 ,

$$T_{2} = \frac{k+1}{2k}T_{1} + \frac{P_{2}V_{1}}{mc_{p}}$$

$$= \frac{1}{2}T_{1}\left(1 + \frac{1}{k} + \frac{R}{c_{p}}\frac{P_{2}}{P_{1 \text{ below}}}\right)$$
(1)

where $k = c_P / c_V$. We can verify at this point that when the initial pressure difference across the partition is zero, the final state (b) is identical to (a): this is in agreement with eq. (1), where $P_{1 \text{ below}} = P_{1 \text{ above}} (= P_2)$ means that $T_2 = T_1$.

The entropy increase from (a) to (b) is associated only with the ideal gas part of the system,

$$S_{\text{gen,a-b}} = \left(S_{\text{gen,a-b}}\right)_{\substack{\text{gas} \\ \text{originally} \\ \text{partition}}} + \left(S_{\text{gen,a-b}}\right)_{\substack{\text{gas} \\ \text{originally} \\ \text{below} \\ \text{partition}}}$$

$$= \frac{m}{2} c_{\text{p}} \ln \frac{T_2}{T_1} - \frac{m}{2} R \ln \frac{P_2}{P_{1 \text{ above}}} + \frac{m}{2} c_{\text{p}} \ln \frac{T_2}{T_1} - \frac{m}{2} R \ln \frac{P_2}{P_{1 \text{ below}}}$$

$$= m c_{\text{p}} \ln \frac{T_2}{T_1} - \frac{m}{2} R \ln \pi$$

where $\pi = P_2/P_{1 \text{ below}}$ is a given constant. We must prove that the quantity