

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,

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

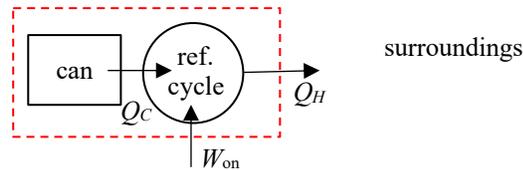
Not part of this reading.

The temperature of a 12 oz (0.354 l) can of soft drink is reduced from 20 °C to 5 °C by a refrigeration cycle. The cycle receives energy by heat transfer from the soft drink and discharges energy by heat transfer at 20 °C to the surroundings. There are no other heat transfers. Determine the minimum theoretical work input required. You may ignore the aluminum can in your calculations.



SOLUTION:

A schematic of the situation is shown below.



Apply the 1st Law to a system consisting of the can and the refrigeration equipment,

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

where,

$$\Delta E_{\text{sys}} = \Delta E_{\text{can}} + \Delta E_{\text{ref. cycle}}, \quad (2)$$

where changes in kinetic and potential energies are ignored for the can so $\Delta E_{\text{can}} = \Delta U_{\text{can}}$. Furthermore, since the refrigeration equipment operates over a cycle, $\Delta E_{\text{ref. cycle}} = 0$. Hence, Eq. (1) becomes,

$$\Delta U_{\text{can}} = -Q_H + W_{\text{on}} \Rightarrow W_{\text{on}} = \Delta U_{\text{can}} + Q_H. \quad (3)$$

The change in the can internal energy is,

$$\Delta U_{\text{can}} = mc(T_{\text{can, f}} - T_{\text{can, i}}), \quad (4)$$

where the soft drink is modeled as an incompressible substance since it's a liquid. The parameter m is the mass of the can and c is its specific heat.

The heat transferred out of the system may be found by applying the 2nd Law,

$$\Delta S_{\text{sys}} = \int_{1,b}^2 \frac{\delta Q_{\text{into}}}{T} + \sigma = \frac{-Q_H}{T_H} + \sigma \Rightarrow Q_H = T_H \sigma - T_H \Delta S_{\text{sys}}, \quad (5)$$

where,

$$\Delta S_{\text{sys}} = \Delta S_{\text{can}} + \Delta S_{\text{ref. cycle}}. \quad (6)$$

Since the refrigeration equipment operates on a cycle, $\Delta S_{\text{ref. cycle}} = 0$. The absolute temperature at the boundary of the system where the heat is transferred out of the system is T_H and σ is the entropy produced during the process due to irreversibilities.

Substituting Eq. (5) into Eq. (3) and simplifying gives,

$$W_{\text{on}} = \Delta U_{\text{can}} + T_H \sigma - T_H \Delta S_{\text{sys}}. \quad (7)$$

Since we're interested in the minimum amount of work required during the process, consider the case when $\sigma = 0$ (an internally reversible process). Recall that $\sigma > 0$ when irreversibilities are present. Since the soft drink is assumed to be an incompressible substance,

$$\Delta S_{\text{can}} = mc \ln \left(\frac{T_{\text{can, f}}}{T_{\text{can, i}}} \right). \quad (8)$$

Substituting Eqs. (4) and (8) into Eq. (7) (with $\sigma = 0$) gives,

$$W_{\text{on,min}} = mc(T_{\text{can},f} - T_{\text{can},i}) - T_H mc \ln\left(\frac{T_{\text{can},f}}{T_{\text{can},i}}\right), \quad (9)$$

$$W_{\text{on,min}} = mc \left[(T_{\text{can},f} - T_{\text{can},i}) - T_H \ln\left(\frac{T_{\text{can},f}}{T_{\text{can},i}}\right) \right]. \quad (10)$$

Using the following parameters,

$$m = (1000 \text{ kg/m}^3)(0.354 \text{ l})(10^{-3} \text{ m}^3/\text{l}) = 0.354 \text{ kg} \quad (\text{assume the density of liquid water})$$

$$c = 4.2 \text{ kJ}/(\text{kg}\cdot\text{K}) \quad (\text{assume the specific heat of liquid water})$$

$$T_{\text{can},f} = 5 \text{ }^\circ\text{C} = 278 \text{ K}$$

$$T_{\text{can},i} = 20 \text{ }^\circ\text{C} = 293 \text{ K}$$

$$T_H = 20 \text{ }^\circ\text{C} = 293 \text{ K}$$

$$\Rightarrow \boxed{W_{\text{in,min}} = 0.591 \text{ kJ}}$$

If we assume the soft drink is a compressed liquid instead of being incompressible, then the change in entropy is,

$$\Delta S_{\text{soda}} = m \Delta s_{\text{soda}} \approx m [s_l(T_{\text{soda},f}) - s_l(T_{\text{soda},i})], \quad (11)$$

where $s_{\text{CL}}(T, p) \approx s_l(T)$. Treating the soda as water and using Table A-2 in Moran et al., 8th ed.,

$$s_l(T_{\text{soda},f} = 5 \text{ }^\circ\text{C}) = 0.0761 \text{ kJ}/(\text{kg}\cdot\text{K}),$$

$$s_l(T_{\text{soda},i} = 20 \text{ }^\circ\text{C}) = 0.2966 \text{ kJ}/(\text{kg}\cdot\text{K}),$$

$$\Rightarrow \Delta S_{\text{soda}} = -0.0781 \text{ kJ}/\text{K},$$

which is identical to the result found using the incompressible substance model.

