Chapter 7

Applications of the Second Law

Advanced Thermodynamics

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7.1 Entropy Changes in Reversible Processes

For reversible process, $\boldsymbol{\delta q_r = du + P\,dv}$

1. Adiabatic process : $\boldsymbol{\delta q_r = 0, ds = 0, s = constant}$
2. Isothermal process : $\boldsymbol{s_2 - s_1 = \int_1^2 \frac{\delta q_r}{T} = \frac{q_r}{T}}$

7.1 Entropy Changes in Reversible Processes

3. Isothermal (and isobaric) change of phase : $s_2 - s_1 = \frac{l}{T}$

4. Isochoric process : $s_2 - s_1 = \int_1^2 c_v \frac{dT}{T} = c_v \ln \frac{T_2}{T_1}$

5. Isobaric process : $\frac{\delta q_r}{T} = \frac{dh}{T} - \frac{v}{T} dP = ds$

$$s_2 - s_1 = \int_1^2 c_p \frac{dT}{T} = c_p \ln \frac{T_2}{T_1}$$

7.2 Temperature-Entropy Diagrams

The total quantity of heat transferred in a reversible process from state 1 to state 2 is given by

$$q_r = \int_1^2 T\,ds$$

The T-s diagram is simple rectangle for a Carnot cycle. The area under the curve is

$$\oint T ds = \sum q_r = w$$

Since $\oint du = 0$

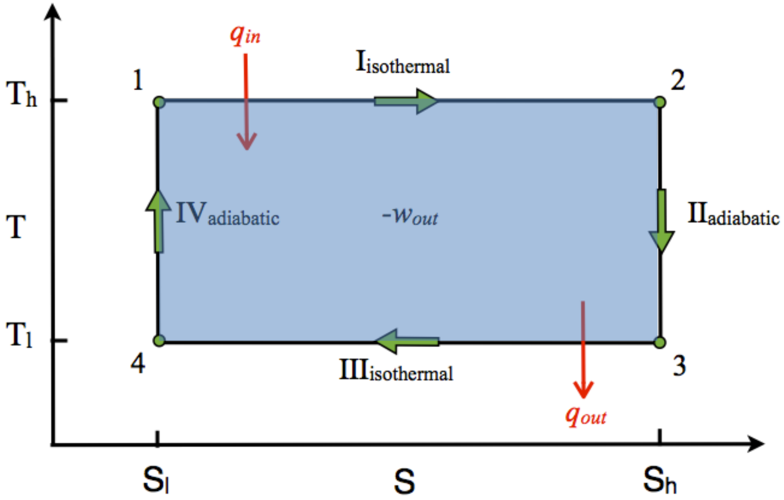


Figure7.1 T-s diagram for a Carnot cycle [1]

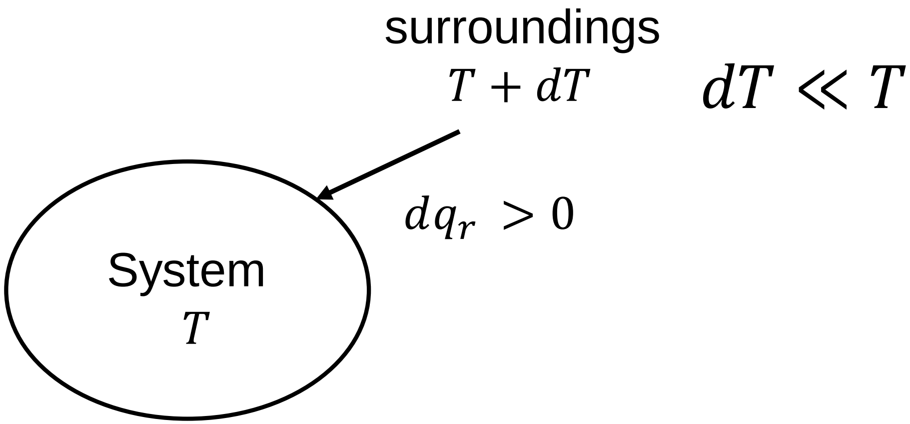
[1] http://juanribon.com/design/carnot-cycle-pv-ts-diagram.php 2017.02.27

7.3 Entropy Change of the Surroundings (Reversible)

The heat flow out of the surroundings at every point is equal in magnitude and opposite in sign to the heat flow into the system.

$$dq_{in} = dq_{out} = dq_r$$

For a reversible process, temperature of system and its surroundings are eqaul



surroundings

$T + dT$

$$dT \ll T$$

$dq_r > 0$

System

T

7.3 Entropy Change of the Surroundings (Reversible)

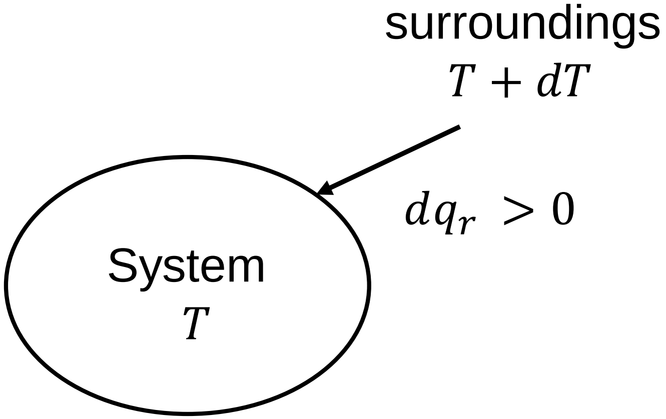
So,

$$\left(\frac{\delta q_r}{T+dT}\right)_{surroundings} \approx \left(\frac{\delta q_r}{T}\right)_{surroundings} = (\delta s)_{surroundings}$$

and from

$$ds_{system} + ds_{surroundings} = ds_{universe},$$

$$|ds|_{surroundings} = -|ds|_{system} \quad \& \quad |ds|_{universe} = 0$$



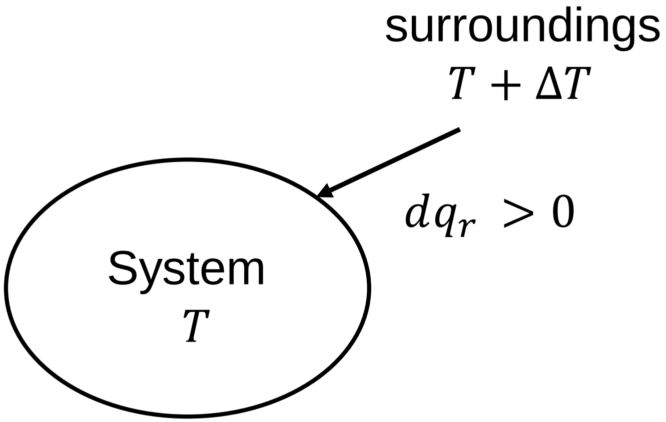
7.3 Entropy Change of the Surroundings (Irreversible)

However for an irreversible case,

$$\Delta T > 0$$

and

$$\boldsymbol{\left(\frac{\delta q_r}{T}\right)_{surroundings} > \left(\frac{\delta q_r}{T+\Delta T}\right)_{surroundings} = (\Delta s)_{surroundings}}$$

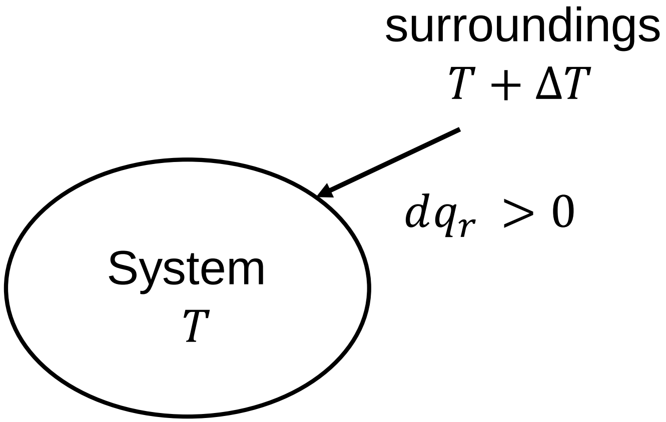


7.3 Entropy Change of the Surroundings (Irreversible)

So,

$$\Delta \boldsymbol{s}_{\boldsymbol{system}} + \Delta \boldsymbol{s}_{\boldsymbol{surroundings}} = \Delta \boldsymbol{s}_{\boldsymbol{universe}} > \mathbf{0}$$

(Entropy generation!)



7.4 Entropy change for an Ideal Gas

With $\boldsymbol{du = c_v dT}$, we have

$$\frac{\overrightarrow{d}q_r}{T} = \frac{c_v dT}{T} + \frac{P}{T}dv = ds$$

For a reversible process, For an ideal gas, P/T = R/v , so

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

Integrating, we have

$$s_2 - s_1 = c_v \, ln \, (\frac{T_2}{T_1}) + R \, ln \, (\frac{v_2}{v_1})$$

7.5 The Tds Equations

From the combined first and second laws, $\mathbf{Tds} = du + P\,dv$

$$Tds = c_p\,dT - T\left(\frac{\partial v}{\partial T}\right)_p dP \qquad (s = s(T, P))$$

(※ Assignments) Entropy can be expressed as function of specific volume and pressure or temperature and specific volume. Prove the below two equations using Maxwell relations.

$$Tds = c_p\left(\frac{\partial T}{\partial v}\right)_p dv + c_v\left(\frac{\partial T}{\partial P}\right)_v dP \quad (s = s(v, P))$$

$$Tds = c_v\,dT + T\left(\frac{\partial P}{\partial T}\right)_v dv \qquad (s = s(T, v))$$

7.5 The Tds Equations

Let $T\ and\ P$ be the independent variables .

The enthalpy is $h \equiv u + P\,v$ thus,

$$\boldsymbol{Tds = dh - vdP}$$

$$\boldsymbol{= [(\frac{\partial h}{\partial T})_P dT + (\frac{\partial h}{\partial P})_T\, dP] - vdP}$$

$$\boldsymbol{ds = \frac{1}{T}(\frac{\partial h}{\partial T})_P dT + \frac{1}{T}[(\frac{\partial h}{\partial P})_T - v]dP}$$

7.5 The Tds Equations

With $s = s(T,P)$, we have

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP$$

$$ds = \frac{1}{T}\left(\frac{\partial h}{\partial T}\right)_P dT + \frac{1}{T}\left[\left(\frac{\partial h}{\partial P}\right)_T - v\right] dP$$

Since $T\ and\ P$ are independent, it follows that

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial h}{\partial T}\right)_P \qquad and \qquad \left(\frac{\partial s}{\partial T}\right)_T = \frac{1}{T}\left[\left(\frac{\partial h}{\partial P}\right)_T - v\right]$$

7.5 The Tds Equations

The differential ds is exact. Therefore,

$$\left[\frac{\partial}{\partial P}\left(\frac{\partial s}{\partial T}\right)_P\right]_T = \frac{\partial^2 s}{\partial P \partial T} = \frac{\partial^2 s}{\partial T \partial P} = \left[\frac{\partial}{\partial P}\left(\frac{\partial s}{\partial T}\right)_T\right]_P$$

Substituting last two Equations from previous slide, we get

$$\frac{1}{T}\frac{\partial^2 h}{\partial P \partial T} = \frac{1}{T}\left[\frac{\partial^2 h}{\partial T \partial P} - \left(\frac{\partial v}{\partial T}\right)_P\right] - \frac{1}{T^2}\left[\left(\frac{\partial h}{\partial P}\right)_T - v\right]$$

$$\leftrightarrow \left(\frac{\partial h}{\partial P}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_P + v$$

7.5 The Tds Equations

For a reversible process $c_P = \left(\frac{\partial h}{\partial T}\right)_P$

$$\boldsymbol{Tds = c_P dT - T\left(\frac{\partial v}{\partial P}\right)_P dP}$$

Finally, since $\beta v = \left(\frac{\partial v}{\partial T}\right)_P$ we have

$$\boldsymbol{Tds = c_P dT - T\, v\beta dP}$$