

Chapter 7

Applications of the Second Law

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7.1 Entropy Changes in Reversible Processes

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

1. Adiabatic process : $\delta q_r = 0, ds = 0, s = \text{constant}$

2. Isothermal process : $s_2 - s_1 = \int_1^2 \frac{\delta q_r}{T} = \frac{q_r}{T}$

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 $\oint du = 0$

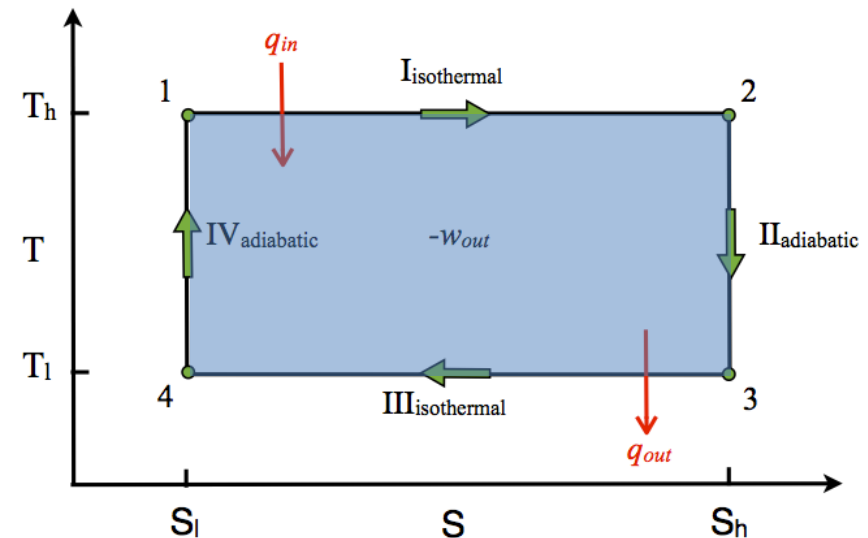


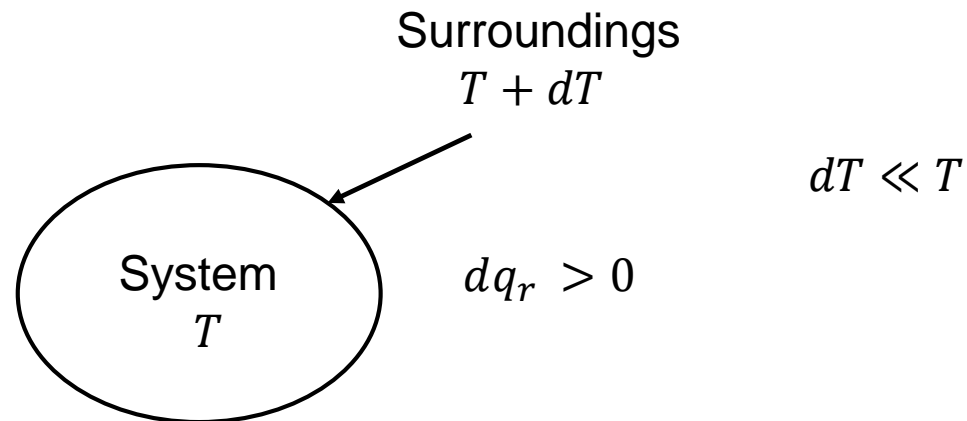
Figure 7.1 T-s diagram for a Carnot cycle [1]

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 equal.



7.3 Entropy Change of the Surroundings (Reversible)

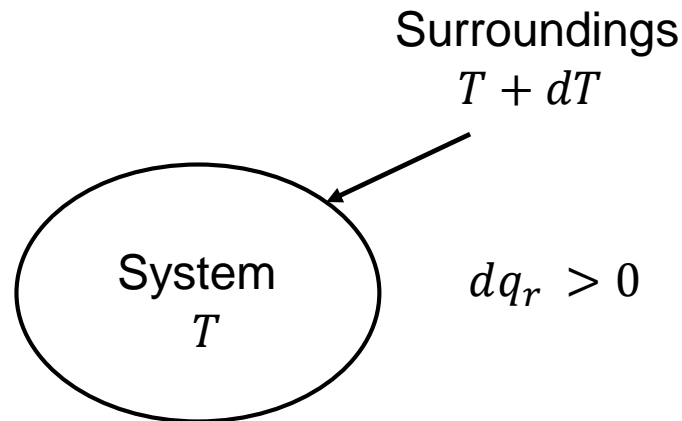
So,

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

and from

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

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



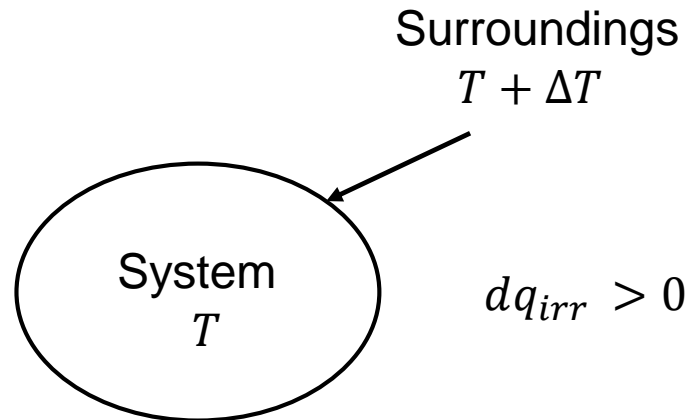
7.3 Entropy Change of the Surroundings (Irreversible)

However for an irreversible case,

$$\Delta T > 0$$

and

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

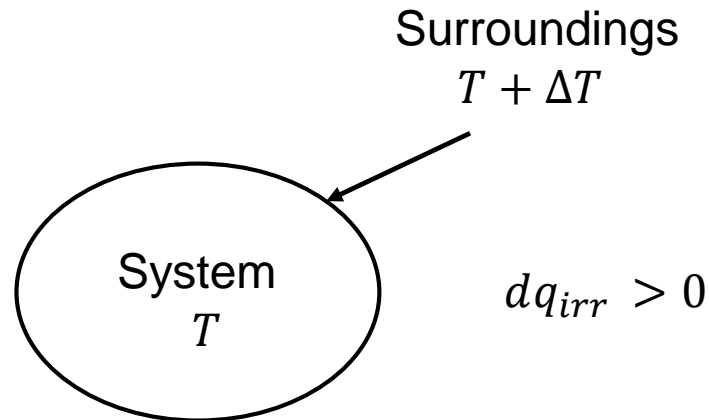


7.3 Entropy Change of the Surroundings (Irreversible)

So,

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{universe}} > 0$$

(Entropy generation!)



7.4 Entropy Change for an Ideal Gas

With $du = c_v dT$, we have

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

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

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

7.5 The Tds Equations

From the combined first and second laws, $Tds = du + P dv$

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

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

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

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

7.5 The Tds Equations

Let T and P be the independent variables .

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

$$Tds = dh - v dP$$

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

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

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

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

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 $c_P = \left(\frac{\partial h}{\partial T}\right)_P$

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

Finally, since the coefficient of volume expansion $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P$, we have

$$Tds = c_P dT - T v \beta dP$$

Chapter 8

Thermodynamic Potentials

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8.1 Introduction

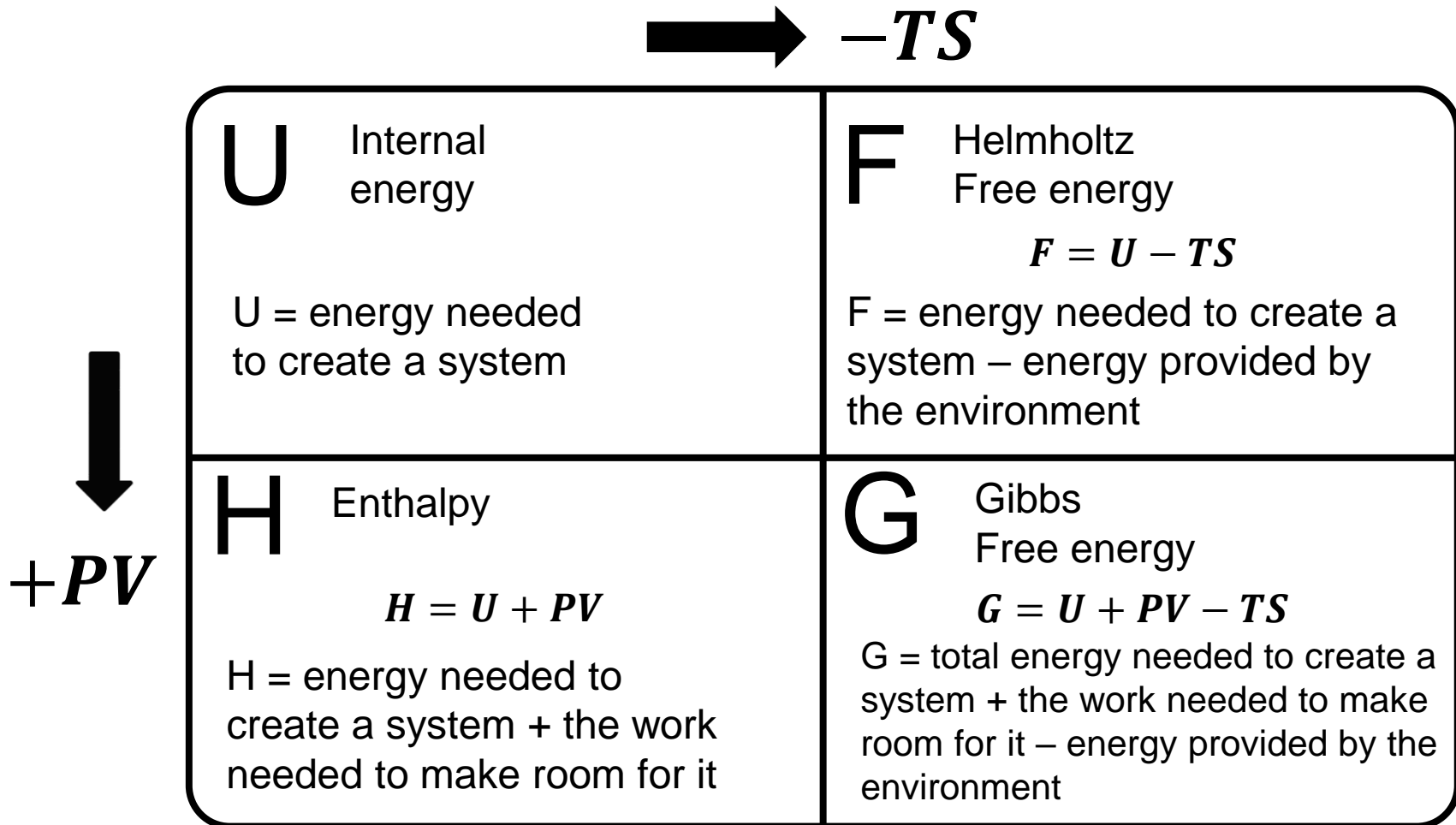


Figure 8.1 Pictorial summary of the four dynamic properties [1]

8.1 Introduction

$$dU = TdS - PdV$$

S and V : intrinsically extensive quantities

T and -P : intensive variables that are said to be canonically conjugate to them

So, canonically conjugate pairs are

$$T, S \text{ and } -P, V$$

T and S are thermal variables, whereas *P and V* are mechanical variables

8.1 Introduction

Assume $U = U(S, V)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\begin{array}{ccc} & \uparrow & \uparrow \\ \left(\frac{\partial U}{\partial S}\right)_V = T, & & \left(\frac{\partial U}{\partial V}\right)_S = -P \end{array}$$

However, the selection of the two independent variables is a matter of choice.

8.3 Definition of the Thermodynamic Potentials

$$H = U + PV$$

$$dH = TdS + VdP$$

Assume $H = H(S, P)$

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T,$$

$$\left(\frac{\partial H}{\partial P}\right)_S = V$$

8.3 Definition of the Thermodynamic Potentials

$$F = U - ST$$

$$dF = -PdV - SdT$$

Assume $F = F(T, V)$

$$dF = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT$$

$$\left(\frac{\partial F}{\partial V}\right)_T = -P, \quad \left(\frac{\partial F}{\partial T}\right)_V = -S$$

8.3 Definition of the Thermodynamic Potentials

$$G = U + PV - ST$$

$$dG = -SdT + VdP$$

Assume $G = G(T, P)$

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

$$\left(\frac{\partial G}{\partial T}\right)_P = -S,$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

8.4 The Maxwell Relations

Each of the four thermodynamic potentials is a state variable whose differential is exact. As an example, we consider

$$dU = TdS + (-P)dV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial P}{\partial S}\right)_V$$

Maxwell relation : $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

8.5 The Helmholtz Function

Change in U is the heat flow in an **isochoric reversible process**.

$$dU = TdS + (-P)dV \quad \rightarrow \quad \Delta U = Q_{Supplied}$$

Change in H is the heat flow in an **isobaric reversible process**.

$$dH = TdS + VdP \quad \rightarrow \quad \Delta H = Q_{Supplied}$$

8.5 The Helmholtz Function

For isothermal process, change in F

$$dF = -SdT - PdV \quad \rightarrow \quad \Delta F = - \int PdV$$

(Work done on/by the system)

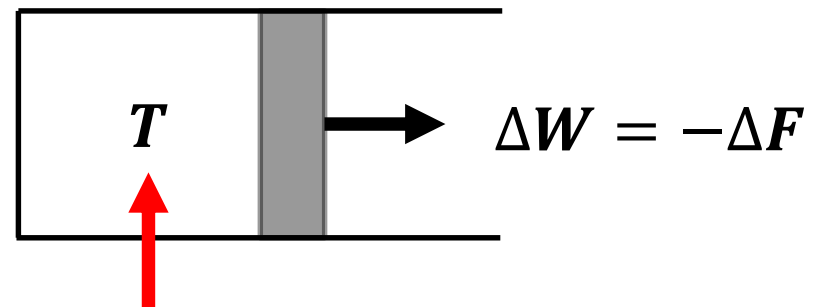
$$\delta Q = dU + \delta W = dU + PdV \quad dS = \frac{\delta Q}{T} + \delta\Theta$$

$$\delta W = -dU + TdS - T\delta\Theta = -d(U - TS) - T\delta\Theta = -dF - T\delta\Theta$$

ΔF = Maximum energy available for work in the isothermal process

$$\Delta W \leq -\Delta F$$

(no change in T)



Q to System

8.6 The Gibbs Function

Consider a system in a surrounding environment that constitutes a temperature and pressure reservoir. Most chemical reactions and some phase changes take place in this way.

$$dG = -SdT + VdP$$

$$\text{If } T = \text{Constant}, P = \text{Constant}, \quad \Delta G)_{T,P} = 0$$

8.6 The Gibbs Function

$$\begin{aligned}\delta W &= PdV + \delta W_{non-mechanical} \\ &= -dU + \delta Q = -dU + TdS - T\delta\Theta\end{aligned}$$

$$\begin{aligned}\delta W_{non-mechanical} &= -dU - PdV + TdS - T\delta\Theta \\ &= -d(U + PV - TS) - T\delta\Theta = -dG - T\delta\Theta\end{aligned}$$

$$\Delta W_{non-mechanical} \leq -\Delta(U + PV - TS) = -\Delta G$$

ΔG = Maximum energy available for work
in the isothermal, isobaric process

