Chapter 8

Thermodynamic Potentials

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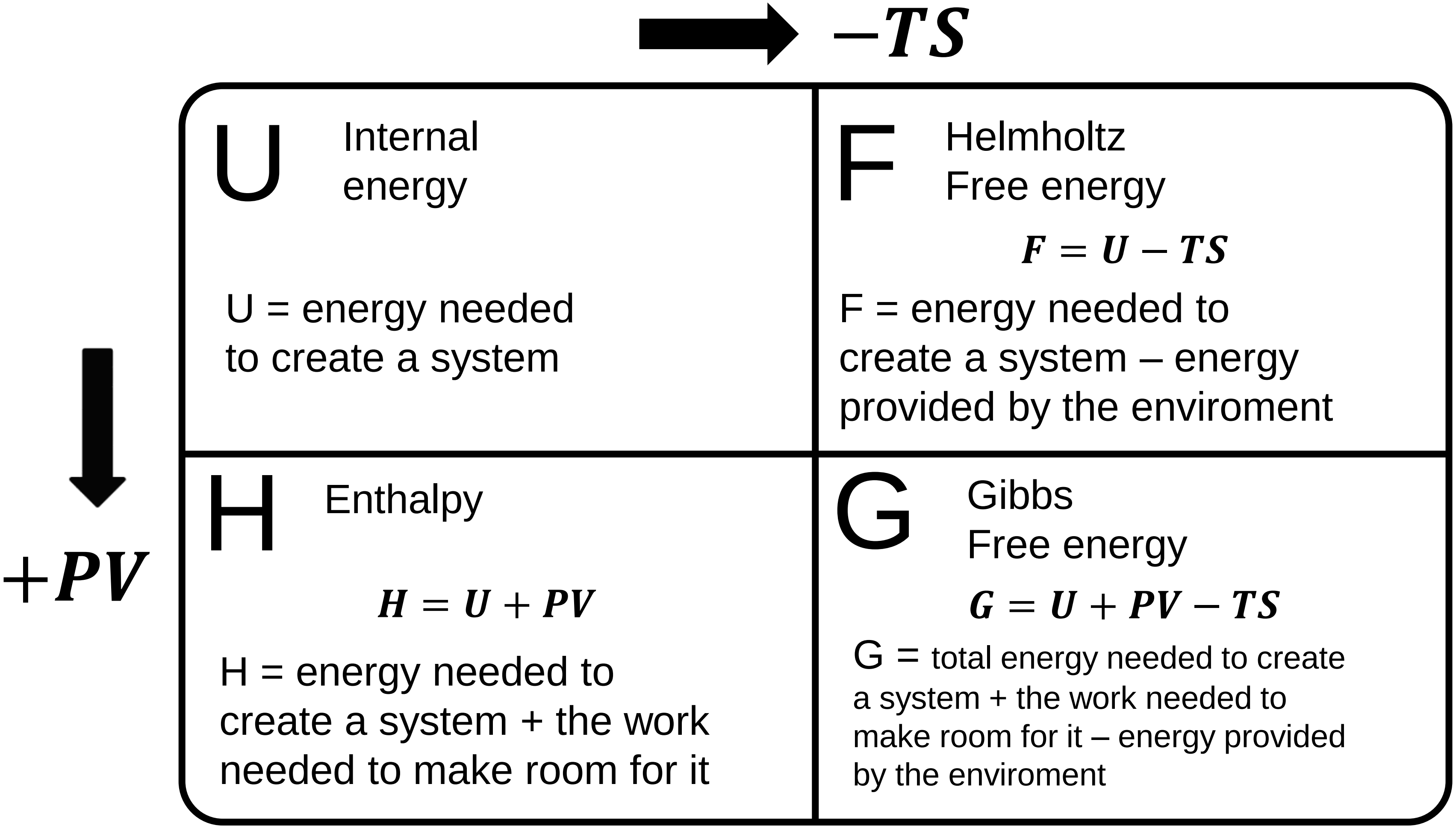
8.1 Introduction



$$-TS$$

$$+PV$$

U Internal energy

U = energy needed to create a system

F Helmholtz Free energy

$$F = U - TS$$

F = energy needed to create a system – energy provided by the enviroment

H Enthalpy

$$H = U + PV$$

H = energy needed to create a system + the work needed to make room for it

G Gibbs Free energy

$$G = U + PV - TS$$

G = total energy needed to create a system + the work needed to make room for it – energy provided by the enviroment

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

[1] R. O'Hayre, S. Cha, W. Colella, F. Prinz, Fuelcell Fundamentals 3rd ed. 30p (2006)

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 by nature mechanical variables

$$S, V \qquad S, P \qquad T, V \qquad T, P$$

8.1 Introduction

Assume $\boldsymbol{U = U(S, V)}$

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

$$\left(\frac{\partial U}{\partial S}\right)_v = T\,, \qquad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

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

8.3 Definition of the Thermodynamic Potentials

$$H = U + PV$$

$$dH = TdS + VdP$$

Assume $H = H(S, P)$

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

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

8.3 Definition of the Thermodynamic Potentials

$$F = U - ST$$

$$dF = -PdV - SdT$$

Assume $F = F(T, V)$

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

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

8.3 Definition of the Thermodynamic Potentials

$$G = U + PV - ST$$

$$dG = -SdT + VdP$$

Assume $\quad \mathbf{G} = G(T, P)$

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

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

8.4 The Maxwell Relations

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

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

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

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

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

Change in F

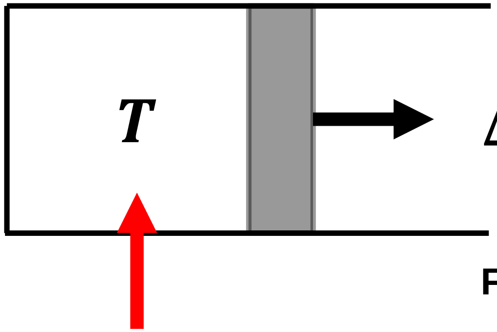
$$dF = -SdT - PdV \quad \rightarrow \quad \Delta F = -\int PdV$$

(Work done on/by the system)

$\Delta F =$ Maximum energy available for work in the isothermal process

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

(no change in T)



$$\Delta W = -\Delta F$$

$Q \;\; from\ System$

Figure 8.2 Piston

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.

$$dG = -SdT + VdP$$

$$If, T = P = Const. \quad \Delta G)_{T,P} \leq 0$$

$$\frac{\delta T}{T} \leq dS \qquad \rightarrow \qquad \delta Q = \Delta U + PdV - TdS \leq 0$$

8.6 The Gibbs Function

Change in G

$$TdS \geq dU + PdV + \Delta W_{non-mech}$$

$$\Delta W_{non-mech} \leq -(\Delta U + P\Delta V - T\Delta S) = -\Delta G$$

$\Delta G =$ Maximum energy available for work in the isothermal, isobaric process

$$\Delta W_{nm} \leq -\Delta G$$

(no change in T, P)

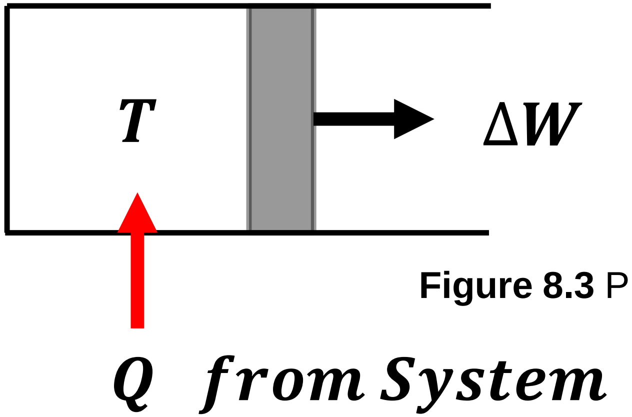


Figure 8.3 Piston