

## Chapter 8

# Thermodynamic Potentials

Min Soo Kim

Seoul National University

# 8.1 Introduction

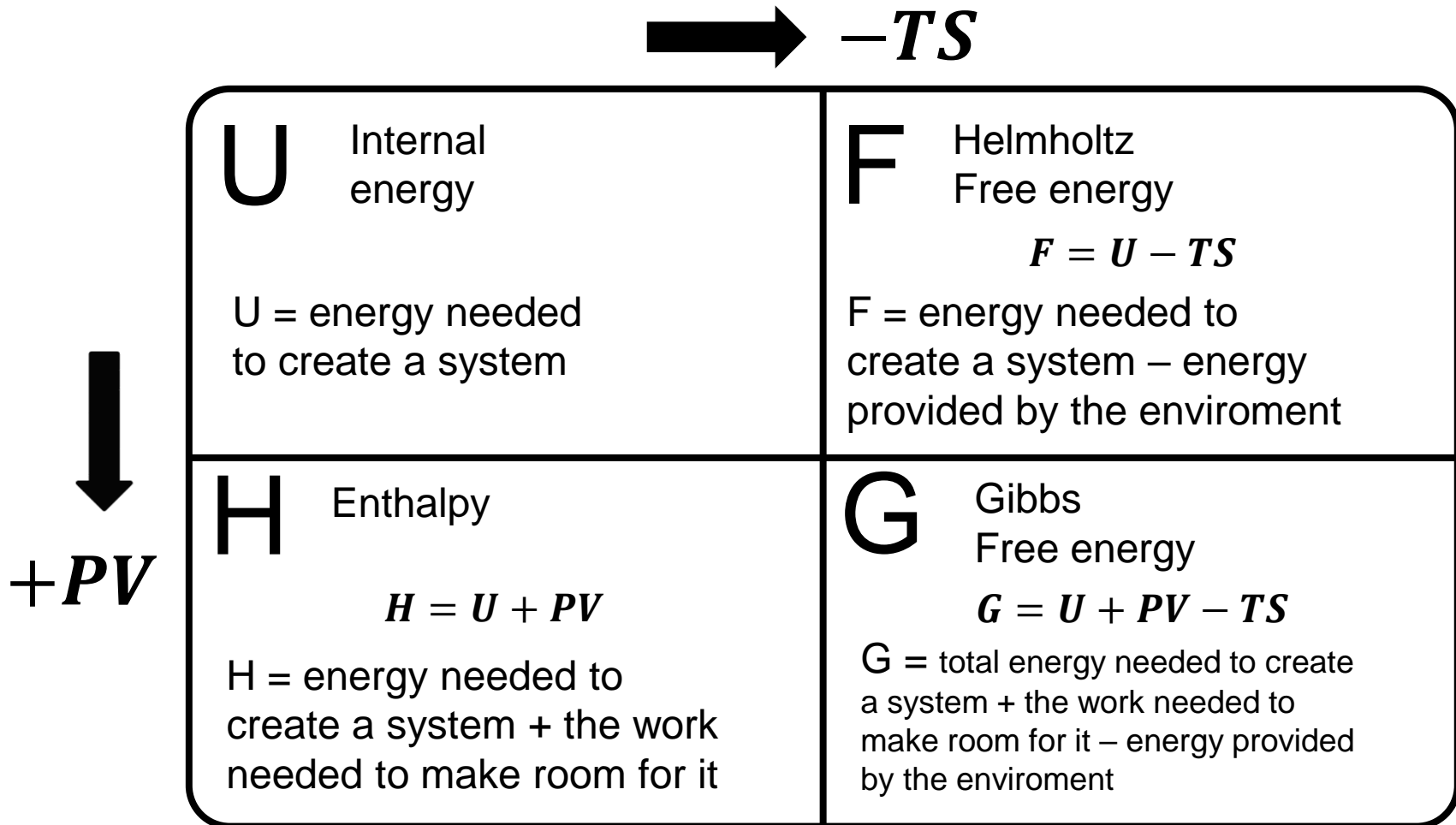


Figure 8.1 Pictorial summary of the four dynamic properties [1]

[1] R. O'Hayre, S. Cha, W. Colella, F. Prinz, Fuelcell Fundamentals 3<sup>rd</sup> 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

$$S, V \quad S, P \quad T, V \quad T, P$$

# 8.1 Introduction

Assume  $U = U(S, V)$

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

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


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  $F = F(T, V)$

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

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

$$\left(\frac{\partial F}{\partial T}\right)_V = -S$$

## 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**

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

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

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

# 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  $T$ )

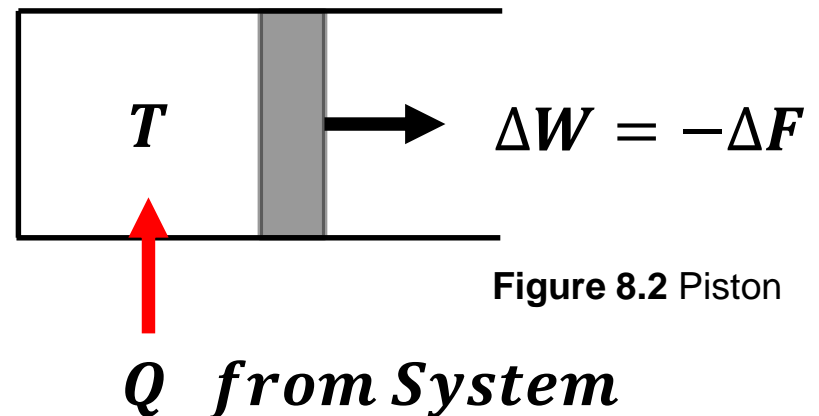


Figure 8.2 Piston

## 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.

$$dG = -SdT + VdP$$

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

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

## 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

$$\Delta W_{nm} \leq -\Delta G \text{ (no change in } T, P)$$