

Chapter 8

Thermodynamic Potentials

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8.1 Introduction

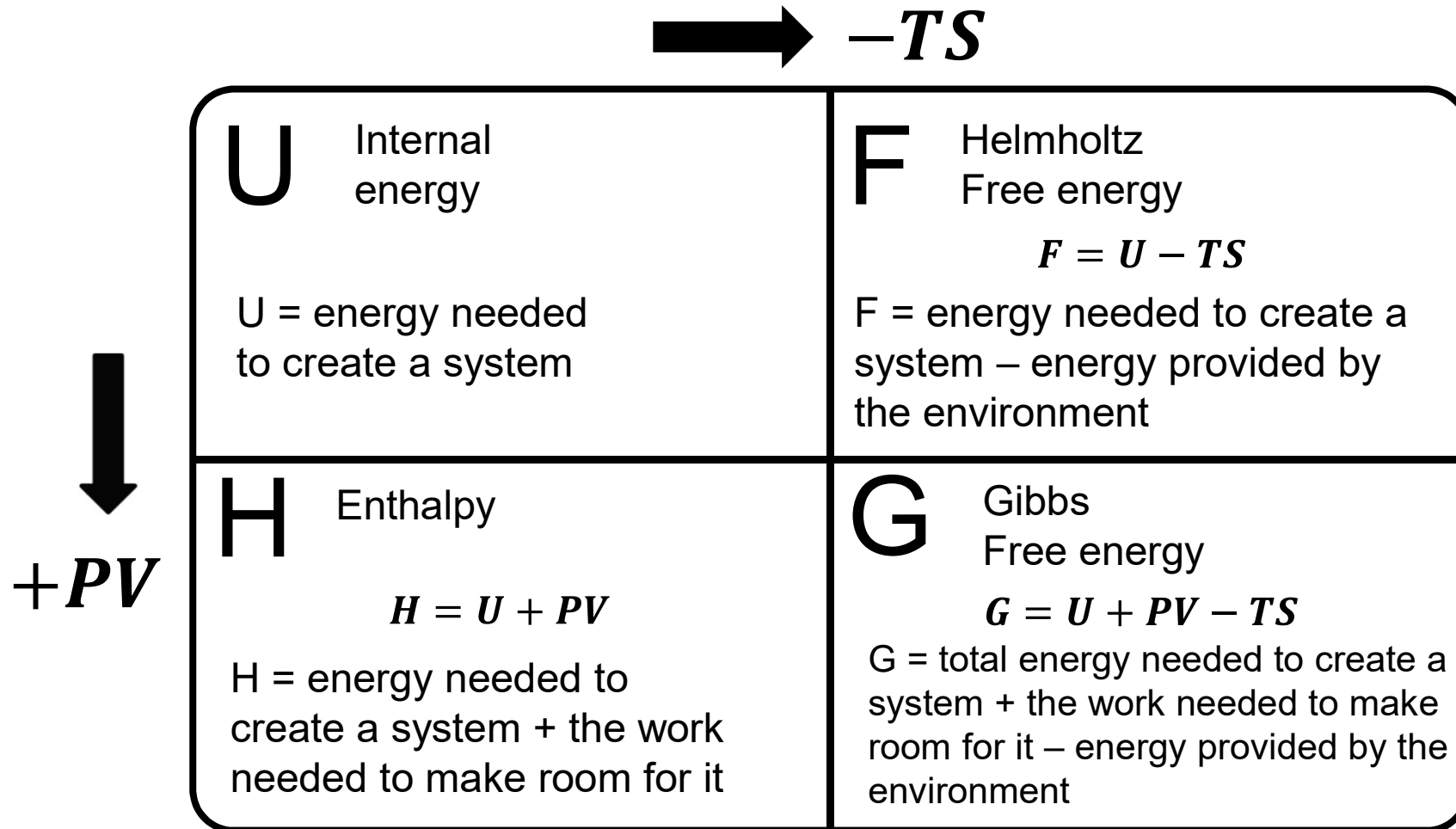


Figure 8.1 Pictorial summary of the four dynamic properties [1]

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 $U = U(S, V)$

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

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

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 $H = H(S, P)$

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

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

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 $G = G(T, P)$

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

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

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

For isothermal process, change in F

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

(Work done on/by the system)

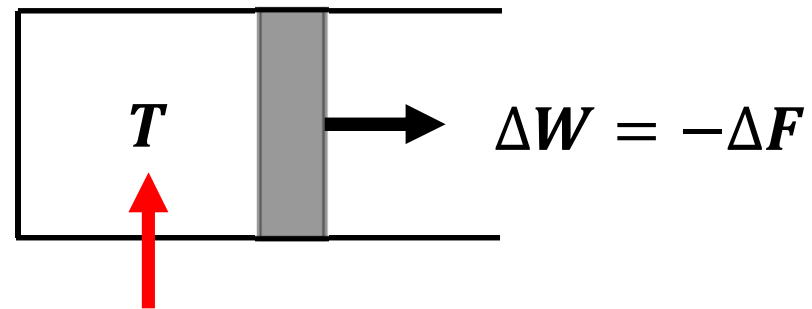
$$\delta Q = dU + \delta W = dU + PdV \quad dS = \frac{\delta Q}{T} + \delta\Theta$$

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

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

