

# PHYS 10352

## PART I: CLASSICAL THERMODYNAMICS

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# WEEK 5: THERMODYNAMIC POTENTIALS

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## RECAP

- ▶ The Clausius inequality states that **over a cycle**:  $\oint \frac{dQ}{T} \leq 0$
- ▶ The quantity  $\frac{dQ}{T}$  is path independent, i.e. it is a **function of state**.
- ▶ We define this function of state as the *entropy*,  $S$ , where

$$\Delta S = S(B) - S(A) = \int_A^B \frac{dQ_{rev}}{T} \geq 0$$

- ▶ Entropy is defined in terms of **reversible processes**.
- ▶ The entropy of an isolated system can only increase or stay the same.
- ▶ An isolated system at equilibrium must be in a state of maximum entropy.
- ▶ We can define heat capacity in terms of entropy.
- ▶ From the first law, we can use entropy to define **the fundamental thermodynamic relation**:

$$dE = T dS + dW_{rev}$$

## SPONTANEOUS PROCESSES

So far we have considered isolated systems and found that they are at equilibrium at maximum entropy. For example, a hot and cold block brought into thermal contact will exchange heat until they are at the same temperature, and not stop half way. This is known as a *spontaneous process*.

But what about non-isolated systems?

Consider a (non-isolated) thermodynamic system at room temperature and pressure, i.e.  $T = T_0, P = P_0$ , which is not in equilibrium. From the 2nd Law, we know that

$$\Delta S_{\text{Universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$

We can write this as

$$\Delta S_{\text{Universe}} = \Delta S - \frac{Q}{T_0} = \frac{1}{T_0} (T_0 \Delta S - \Delta E - P_0 \Delta V) = -\frac{1}{T_0} (\Delta E - T_0 \Delta S + P_0 \Delta V) \geq 0$$

and therefore

$$(\Delta E - T_0 \Delta S + P_0 \Delta V) = \Delta(E - T_0 S + P_0 V) = \Delta A \leq 0,$$

where  $A$  is known as the *availability* of the system.

During any spontaneous change of a system at constant temperature and pressure:  $\Delta A \leq 0$ .

# SPONTANEOUS PROCESSES

System	$\Delta E = 0, \Delta V = 0$	$\Delta T = 0, \Delta V = 0$	$\Delta T = 0, \Delta P = 0$
Direction of spontaneous change	$\Delta S \geq 0$	$\Delta F \leq 0$	$\Delta G \leq 0$
Equilibrium achieved when	$\Delta S = 0$	$\Delta F = 0$	$\Delta G = 0$

# THERMODYNAMIC POTENTIALS

## HELMHOLTZ FREE ENERGY

$$F(T, V) = E - TS$$

Where does it come from?

$$\begin{aligned}dE &= TdS - PdV, \\ &= TdS + \underbrace{SdT - SdT}_{=0} - PdV, \\ &= d(TS) - SdT - PdV, \\ \Rightarrow d(E - TS) &= -SdT - PdV.\end{aligned}$$

It tells us that:

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

# THERMODYNAMIC POTENTIALS

## HELMHOLTZ FREE ENERGY

$$F(T, V) = E - TS$$

Consider changes that happen at constant volume and constant temperature:

$$\begin{aligned}d(E - TS) &= dE - TdS - SdT \\ &= dE - TdS \quad (\text{constant } T) \\ &= dE - TdS \leq 0 \quad (\text{constant } V)\end{aligned}$$

Therefore the Helmholtz energy,  $dF \leq 0$ , for spontaneous processes that happen at constant temperature and volume, i.e. it is a decreasing quantity that becomes zero at equilibrium.

# THERMODYNAMIC POTENTIALS

## HELMHOLTZ FREE ENERGY

$$F(T, V) = E - TS$$

Consider changes that happen at constant volume and constant temperature:

$$\begin{aligned}d(E - TS) &= dE - TdS - SdT \\ &= dE - TdS \quad (\text{constant } T) \\ &= \bar{d}W_{\text{rev}} \quad (TdS = \bar{d}Q_{\text{rev}})\end{aligned}$$

The maximal non-volume reversible work that can be done in a constant volume and constant temperature process is given by  $dF$ .



# THERMODYNAMIC POTENTIALS

## GIBBS FREE ENERGY

$$G(T, P) = E - TS + PV$$

Where does it come from?

$$\begin{aligned}d(E - TS) &= -SdT - PdV, \\ &= -SdT + VdP \underbrace{- VdP - PdV}_{=-d(PV)}, \\ \Rightarrow d(E - TS + PV) &= -SdT + VdP.\end{aligned}$$

It tells us that:

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

# THERMODYNAMIC POTENTIALS

## GIBBS FREE ENERGY

$$G(T, P) = E - TS + PV$$

Consider changes that happen at constant pressure and constant temperature:

$$\begin{aligned}d(E - TS + PV) &= dE - TdS - SdT + PdV + VdP \\ &= dE - TdS + PdV \quad (\text{constant } T \text{ \& constant } P) \\ &= dE - TdS + PdV \leq 0 \quad (dS \geq dQ_{\text{rev}}/T)\end{aligned}$$

Therefore the Gibbs free energy,  $dG \leq 0$ , for processes that happen at constant temperature and pressure, i.e. it is a decreasing quantity that becomes zero at equilibrium.

# THERMODYNAMIC POTENTIALS

## GIBBS FREE ENERGY

$$G(T, P) = E - TS + PV$$

Consider changes that happen at constant pressure and constant temperature:

$$\begin{aligned}d(E - TS + PV) &= \underbrace{dE - TdS - SdT}_{\bar{d}W_{\text{rev}}} + \underbrace{PdV}_{-\bar{d}W_{\text{vol}}} + VdP \\ &= \bar{d}W_{\text{rev}} - \bar{d}W_{\text{vol}} \quad (\text{constant } T \text{ \& constant } P) \\ &= \bar{d}W_{\text{other}}\end{aligned}$$

The maximum non-volume reversible work that can be done in a constant pressure and constant temperature process is given by  $dG$ .

# THERMODYNAMIC POTENTIALS

## ENTHALPY

$$H(P, S) = E + PV$$

Where does it come from?

$$\begin{aligned}d(E - TS + PV) &= -SdT + VdP \\ &= \underbrace{-SdT - TdS}_{=-d(TS)} + TdS + VdP \\ \Rightarrow d(E + PV) &= TdS + VdP.\end{aligned}$$

It tells us that:

$$T = \left( \frac{\partial H}{\partial S} \right)_P \quad \text{and} \quad V = \left( \frac{\partial H}{\partial P} \right)_S.$$

# THERMODYNAMIC POTENTIALS

## ENTHALPY

$$H(S, P) = E + PV$$

Consider changes that happen at constant entropy and constant pressure:

$$\begin{aligned}d(E + PV) &= dE + PdV + VdP \\ &= dE + PdV \quad (\text{constant } P)\end{aligned}$$

Therefore spontaneous processes can happen when  $\Delta H$  is either positive or negative.

## ORDER OF DERIVATION

$$E \longrightarrow F \longrightarrow G \longrightarrow H$$

# THERMODYNAMIC POTENTIALS

## DIRECTION OF SPONTANEOUS CHANGE

$$H(P, S) = E + PV$$

$$G(T, P) = E - TS + PV$$

Therefore

$$\begin{aligned} dG &= dE - TdS - SdT + PdV + VdP \\ &= dH - TdS \leq 0 \end{aligned} \quad (\text{constant } T \text{ \& constant } P)$$

- ▶ If  $\Delta G < 0$  then the process can happen spontaneously.
- ▶ If  $\Delta G > 0$  then the process cannot happen spontaneously unless it is activated, i.e. by a coupled process where  $\Delta G < 0$ .
- ▶ If  $\Delta G = 0$  then the system is in equilibrium.

## THERMODYNAMIC POTENTIALS

### WORKED EXAMPLE - $\text{NH}_4\text{Cl}$

Consider the reaction:



At room temperature and pressure, the enthalpy of this reaction is  $\Delta H = -176.2 \text{ kJ}$  and the change in entropy is  $\Delta S = -0.285 \text{ kJ/K}$ .

- (a) Is this a spontaneous reaction?
- (b) At what temperature will the direction of the spontaneous reaction reverse?
- (c) State your assumptions.



## THERMODYNAMIC POTENTIALS

### WORKED EXAMPLE - $\text{NH}_4\text{Cl}$

Consider the reaction:



At room temperature and pressure, the enthalpy of this reaction is  $\Delta H = -176.2 \text{ kJ}$  and the change in entropy is  $\Delta S = -0.285 \text{ kJ/K}$ .

- (a) Is this a spontaneous reaction?
- (b) At what temperature will the direction of the reaction reverse?
- (c) State your assumptions.

(a) A process will happen spontaneously when  $\Delta G < 0$ . So we need to calculate

$$\Delta G = \Delta H - T\Delta S = -176.2 - 293 \cdot (-0.285) = -92.7 \text{ kJ}$$

Therefore the reaction will proceed spontaneously.

(b) The direction of the reaction will reverse when  $\Delta G > 0$ .

$$0 = \Delta H - T\Delta S = -176.2 + T \cdot (-0.285) \Rightarrow T = \Delta H / \Delta S = -176.2 / -0.285 = 618.2 \text{ K.}$$

(c) Assumptions:  $\Delta H$  and  $\Delta S$  are not temperature dependent.

# INTERPRETATION OF THE POTENTIALS

INTERNAL ENERGY  $E(S, V)$

If a system is thermally isolated ( $Q = 0$ ), then the change in availability becomes

$$\Delta A = \Delta E + P_0 \Delta V = 0.$$

This is just a statement of the first law in adiabatic processes;

$$\Delta E = -P_0 \Delta V.$$

We simply have that the change in internal energy is equivalent to the work done on the system. Therefore, the internal energy is minimised within the constraints of the system.

# INTERPRETATION OF THE POTENTIALS

## ENTROPY $S(E, V)$

If the system is thermally isolated at a fixed volume, no heat can enter it and it can do no work. Therefore, both  $E$  and  $V$  are constant. In this case, the change in availability becomes

$$\Delta A = -T_0 \Delta S.$$

Leaving us with,

$$(\Delta S)_{E,V} \geq 0,$$

as expected. All spontaneous changes of this type reach equilibrium when entropy is maximised.

## INTERPRETATION OF THE POTENTIALS

HELMHOLTZ FREE ENERGY  $F(T, V) = E - TS$

If the system undergoes a process that starts and ends at the same temperature and which is at a constant volume, the change in availability becomes

$$\Delta A = \Delta (E - T_0 S) = \Delta F.$$

Therefore a spontaneous change will reduce the Helmholtz free energy;

$$\boxed{(\Delta F)_{T,V} \leq 0.}$$

Hence equilibrium will be reached when  $F(T, V)$  is minimised. Though the total volume is constant, there could be *internal variables* that are free to change whilst approaching equilibrium.

## INTERPRETATION OF THE POTENTIALS

GIBBS FREE ENERGY  $G(T, P) = F + PV = E - TS + PV$

If the system undergoes a process that starts and ends at the same temperature and pressure, the change in availability becomes

$$\Delta A = \Delta (E - T_0S + P_0V) = \Delta G.$$

Therefore a spontaneous change will reduce the Gibbs free energy;

$$(\Delta G)_{T,P} \leq 0.$$

In this case, at equilibrium, the Gibbs free energy will be minimised;

$$(\Delta G)_{T,P} = 0.$$

## INTERPRETATION OF THE POTENTIALS

ENTHALPY  $H(S, P) = E + PV$

For a system at a constant pressure,  $P_0$ , the work done by the system is  $P_0\Delta V$ . From the first law,

$$\Delta E = Q - P_0\Delta V.$$

The change in enthalpy in this process is,

$$\Delta H = \Delta E + P_0\Delta V,$$

therefore

$$\boxed{(\Delta H)_P = Q;}$$

at constant pressure, the change in enthalpy is equal to the heat.

Note this is always an equality. If the only way to do work is by changing the volume, then the change in enthalpy is the heat released by the system. This is why it is often used in chemistry to study reactions or phase changes.

## WORKED EXAMPLE - H<sub>2</sub>O

At atmospheric temperature and pressure, the entropy of various molecules is given in the table below. Using this information, calculate the heat released when hydrogen and oxygen combine reversibly to form one mole of water.

If the reaction happens irreversibly, will the heat given out be greater or less?

	$S$ [J K <sup>-1</sup> mol <sup>-1</sup> ]
H <sub>2</sub> (gas)	131
O <sub>2</sub> (gas)	205
H <sub>2</sub> O (liquid)	70

## WORKED EXAMPLE - H<sub>2</sub>O

When hydrogen and oxygen combine at atmospheric temperature and pressure to form one mole of water, the heat given out is  $2.86 \times 10^5$  J. What is the change in Gibbs free energy associated with this process?

If  $\Delta Z$  is the charge that circulates when 1 mole of water is electrolysed into gaseous hydrogen and oxygen, find the minimum voltage that must be applied across the cell for this reaction to proceed.



## MAXWELL RELATIONS

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

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

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

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

The Maxwell relations are derived using the second derivatives of each thermodynamic potential ( $E, F, G, H$ ).

They are useful for *switching between variables*, especially in the case of variables that are not possible to measure directly - like entropy.

## MAXWELL RELATIONS

From the fundamental thermodynamic relation we can write,

$$dE = TdS - PdV = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV.$$

Equating coefficients of  $dS$  and  $dV$ ,

$$T = \left(\frac{\partial E}{\partial S}\right)_V \quad \text{and} \quad P = -\left(\frac{\partial E}{\partial V}\right)_S.$$

As

$$\frac{\partial}{\partial V} \left(\frac{\partial E}{\partial S}\right) = \frac{\partial}{\partial S} \left(\frac{\partial E}{\partial V}\right),$$

then

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

maxwell relation

## MAXWELL RELATIONS

From the Helmholtz free energy we can write,

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

Equating coefficients of  $dT$  and  $dV$ ,

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

As

$$\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V}\right),$$

then

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

maxwell relation

## MAXWELL RELATIONS

From the Gibbs free energy we can write,

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

Equating coefficients of  $dT$  and  $dV$ ,

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

As

$$\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T}\right) = \frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P}\right),$$

then

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

maxwell relation

## MAXWELL RELATIONS

From the Enthalpy we can write,

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

Equating coefficients of  $dT$  and  $dV$ ,

$$T = \left(\frac{\partial H}{\partial S}\right)_P \quad \text{and} \quad V = \left(\frac{\partial H}{\partial P}\right)_S.$$

As

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

then

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

maxwell relation

# MAXWELL RELATIONS

## WORKED EXAMPLE - IDEAL GAS

By considering the change in energy density of an ideal gas at constant temperature, use the Maxwell relations to show that  $P \propto T$  for an ideal gas at fixed volume.

For an ideal gas we know that  $E \equiv E(T)$  and therefore  $(\partial E / \partial V)_T = 0$ .

From the fundamental thermodynamic relation, we can write:

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P = 0.$$

Using the Maxwell relation

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

we can rewrite this as

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P = 0.$$

Rearranging, we find

$$T \left(\frac{\partial P}{\partial T}\right)_V = P \quad \Rightarrow \quad \frac{dP}{P} = \frac{dT}{T} \quad \Rightarrow \quad P \propto T$$

as required.

## MAXWELL RELATIONS

### WORKED EXAMPLE - PHOTON GAS

A photon gas has an equation of state:  $P = \frac{1}{3}u$ , where  $u$  is the specific internal energy, i.e. energy density. By considering the method used in the previous worked example, show that for a photon gas,  $E = kVT^4$ , where  $k$  is a constant.

# MAXWELL RELATIONS

## WORKED EXAMPLE - HEAT CAPACITIES

Any heat capacity can be written in the form  $T(dS/dT)$ . By considering the Maxwell relations, use this to show that  $C_p = C_v + nR$ .



## SUMMARY

- ▶ Starting from the fundamental thermodynamic relation we can derive the thermodynamic potentials:

$$F(T, V) = E - TS$$

$$G(T, P) = E - TS + PV$$

$$H(S, P) = E + PV$$

- ▶ Helmholtz free energy,  $F$ , is decreasing for spontaneous processes at constant temperature and volume.
- ▶ Gibbs free energy,  $G$ , determines the direction of spontaneous processes at constant pressure and temperature.
- ▶ The second derivatives of the thermodynamic potentials give us the Maxwell relations:

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

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

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

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