

# Kittel Chapter 8 Notes

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## Definition of Heat and Work

Heat and work are forms of energy transfer. **Heat** is the transfer of energy to a system by thermal contact with a reservoir. **Work** is the transfer of energy to a system by a change in the external parameters that describe the system.

With a system that is in thermal contact with a reservoir at some temperature  $\tau$ , heat would be the energy transfer from the reservoir to the system. There is an associated change in entropy of the system since  $d\sigma = dU/\tau$ . Work does not have an associated change of entropy since it is only the transfer of energy by a change of internal parameters.

A **reversible** process has the total entropy of the interacting systems conserved, while an **irreversible** process has a net gain of total entropy of the interacting systems.

Total energy is conserved, so

$$dU = \bar{d}Q + \bar{d}W = \bar{d}W + \tau d\sigma$$

. The bar through the d in the differentials is because they are not exact. This means that their values are path dependent.

## Conversion of Heat to Work

All types of work are equivalent since they can be converted into each other. Work can also be completely converted into heat. Heat, on the other hand, cannot be completely converted into work since heat increases the entropy of the system and work has no effect on the entropy of the system. The entropy built up from converting heat into work must be expelled as waste heat at a temperature lower than the input heat.

Energy conversion devices often use cycles to allow for entropy to accumulate and then disposed of later. The entropy increases over each cycle and is then dumped later on, so excess entropy doesn't need to be removed immediately.

Let's look at a cycle that has an input heat  $Q_h$  and output heat  $Q_l$ . If it is a reversible process, we would know that the entropy at the input is the same as the entropy at the output.

$$\begin{aligned}\sigma_h &= \sigma_l \\ \frac{Q_h}{\tau_h} &= \frac{Q_l}{\tau_l}\end{aligned}$$

The output heat is then

$$Q_l = \left(\frac{\tau_l}{\tau_h}\right)Q_h$$

The change in heat in this process is equal to the work generated, so

$$W = Q_h - Q_l = \left(\frac{\tau_h - \tau_l}{\tau_h}\right)Q_h$$

We can use this to find the Carnot efficiency, which is the ratio of the generated work to the heat in the reversible process.

$$\eta_C = \left(\frac{W}{Q_h}\right)_{rev} = \frac{T_h - T_l}{T_h}$$

The Carnot efficiency is the highest possible value of the energy conversion efficiency  $\eta$ , which is the ratio of generated work to the input heat of some process. Since most devices involve irreversible processes, we know that

$$\begin{aligned} \sigma_l &\geq \sigma_h \\ Q_l &\geq Q_h \left(\frac{\tau_l}{\tau_h}\right) \\ W = Q_h - Q_l &\leq \left(\frac{\tau_h - \tau_l}{\tau_h}\right) Q_h = \eta_C Q_h \\ \eta = \frac{W}{Q_h} &\leq \frac{\tau_h - \tau_l}{\tau_h} = \eta_C \end{aligned}$$

There are several causes of irreversibility.

1. Some of the heat might bypass the conversion process altogether.
2. Some of the initial temperature difference might be used up due to thermal resistance along the path.
3. Friction might convert some of the work generated back into heat.
4. Irreversible gas expansion that generates no work.

## Refrigerators

A **heat engine** is a device that converts heat into work. A **refrigerator** is a heat engine that is ran in reverse, or use work to move heat from a low temperature to a higher temperature. The important energy ratio for refrigerators is the **coefficient of refrigerator performance**  $\gamma$ .

$$\gamma = \frac{Q_l}{W}$$

In a completely reversible process,  $\gamma = \gamma_C$ .  $\gamma_C$  is called the **Carnot coefficient**. We can find the work as it relates to the heat at low temperature with

$$W = Q_h - Q_l = \left(\frac{\tau_h - \tau_l}{\tau_l}\right) Q_l$$

This gives us a Carnot coefficient of

$$\gamma_C = \left(\frac{Q_l}{W}\right)_{rev} = \frac{T_l}{T_h - T_l}$$

In a refrigerator, the excess entropy due to its irreversibilities are ejected at the higher temperature. This gives us

$$\begin{aligned}\sigma_h &\geq \sigma_l \\ Q_h &\geq \left(\frac{\tau_h}{\tau_l}\right)Q_l \\ W = Q_h - Q_l &\geq \left(\frac{\tau_h}{\tau_l} - 1\right)Q_l = \frac{\tau_h - \tau_l}{\tau_l}Q_l = \frac{Q_l}{\gamma_C}\end{aligned}$$

Which leads to the inequality

$$\gamma = \frac{Q_l}{W} \leq \gamma_C$$

## Air Conditioners and Heat Pumps

Air Conditioners act as heat pumps that push heat from one system into another. You can cool a room by pumping the heat outside, or you can warm a room by pumping the heat inside.

## Carnot Cycle

The **Carnot Cycle** is the simplest process that generates work from heat or how refrigeration works. The cycle involves some substance being compressed and expanded. If we were to start the cycle out at high temperature  $\tau_H$  and low entropy  $\sigma_l$ , the stages of the Carnot cycle will be:

1. The substance is expanded **isothermally** until its entropy reaches  $\sigma_H$ .
2. The substance is expanded **isentropically** until its temperature reaches  $\tau_l$ .
3. The substance is compressed **isothermally** until its entropy reaches  $\sigma_L$ .
4. The substance is compressed **isentropically** until its temperature reaches  $\tau_h$ .

The entropy that changes is the entropy contained in the substance and is related the entropy flow by

$$\sigma_h = \sigma_l = \sigma_H - \sigma_L$$

for the Carnot cycle.

The work done by the system each cycle is the area of the rectangle in the graph of entropy vs. temperature.

$$W = (\tau_h - \tau_l)(\sigma_H - \sigma_L)$$

Since energy is conserved, we know that

$$\oint dU = \oint \tau d\sigma - \oint p dV = 0$$

This leads us to

$$\oint pdV = \oint \tau d\sigma$$

The heat taken up during the first phase of the Carnot cycle is

$$Q_h = \tau_h(\sigma_H - \sigma_L)$$

The Carnot cycle is a good point of comparison for looking at the efficiency of some process. The Carnot cycle is the ideal, or best case scenario cycle, and any real world process will have an efficiency less than the Carnot cycle.

## Example: Carnot Cycle for an Ideal Gas

We start with a monatomic gas with an initial volume  $V_1$  and is in thermal equilibrium with a reservoir  $\mathcal{R}_h$  at temperature  $\tau_h$ . During the **first stage**, the gas is expanded isothermally into a volume  $V_2$  after absorbing heat  $Q_h$  from the reservoir. This absorbed heat is converted into work  $W_{12}$  to push a piston.

$$Q_h = W_{12} = \int pdV = N\tau_h \int \frac{dV}{V} = N\tau_h \ln\left(\frac{V_2}{V_1}\right)$$

For the **second stage**, the gas is disconnected from the reservoir and expands isentropically until the temperature reaches  $\tau_l$ .

$$W_{23} = \Delta U = U(\tau_h) - U(\tau_l) = \frac{3}{2}N(\tau_h - \tau_l)$$

The new volume  $V_3$  at the end of this stage is related to its previous volume by

$$\tau_l V_3^{2/3} = \tau_h V_2^{2/3}$$

$$\frac{V_3}{V_2} = \left(\frac{\tau_h}{\tau_l}\right)^{3/2}$$

For the **third stage**, the gas is brought into contact with reservoir  $\mathcal{R}_l$  at temperature  $\tau_l$  and compressed isothermally to a new volume  $V_4$  chosen to satisfy

$$\frac{V_4}{V_1} = \left(\frac{\tau_h}{\tau_l}\right)^{3/2} = \frac{V_3}{V_2}$$

The work necessary for this compression is

$$W_{34} = N\tau_l \ln\left(\frac{V_3}{V_4}\right) = N\tau_l \ln\left(\frac{V_2}{V_1}\right)$$

This work is ejected into  $\mathcal{R}_l$  as heat  $Q_l$ . For the **fourth stage**, the gas is disconnected from the reservoir  $\mathcal{R}_l$  and compressed isentropically until it returns to the initial temperature  $\tau_h$ . Due to our choice of  $V_4$ , the volume has returned to  $V_1$  so the work done on the gas is then

$$W_{41} = \frac{3}{2}N(\tau_h - \tau_l)$$

This cancels the work done during the isentropic expansion of stage 2  $W_{23}$ . The total work done by the gas is then

$$\begin{aligned} W &= W_{12} + W_{23} - W_{34} - W_{41} = W_{12} - W_{34} \\ &= N(\tau_h - \tau_l) \ln\left(\frac{V_2}{V_1}\right) \end{aligned}$$

The efficiency is given by

$$\eta = \frac{W}{Q_h} = \frac{\tau_h - \tau_l}{\tau_h} = \eta_C$$

## Irreversible Work

If some of the work done on a system is irreversible, the work required to achieve some change is larger than the reversible work.

$$dW_{irr} > dW_{rev}$$

Due to conservation of energy, we know that the total energy is

$$dU = dW_{irrev} + dQ_{irrev} = dW_{rev} + dQ_{rev}$$

This means that the heat transferred in an irreversible process is less than the reversible heat.

$$dQ_{irrev} < dQ_{rev}$$

The increase in entropy for irreversible processes in a system can come from the delivery of work from another system, but it can also occur in pure heat transfer if the two systems are at separate temperatures. For such a system

$$dU_1 = dQ_1 = \tau_1 d\sigma_1$$

$$dU_2 = dQ_2 = \tau_2 d\sigma_2$$

$$dQ_1 + dQ_2 = 0$$

With  $\tau_1 > \tau_2$ , the new entropy is then

$$\begin{aligned} d\sigma_{irrev} &= d\sigma_1 + d\sigma_2 = \frac{dQ_1}{\tau_1} + \frac{dQ_2}{\tau_2} \\ &= \left( \frac{\tau_2 - \tau_1}{\tau_1 \tau_2} \right) dQ_1 \end{aligned}$$

Since  $dQ_1 < 0$  (heat flows from high temperature to low temperature) and  $\tau_2 - \tau_1 < 0$ , the new entropy is positive.

## Example: Sudden Expansion of an Ideal Gas

We are going to look into the sudden expansion of an ideal gas into a vacuum. There is no heat or work transfer which means

$$\begin{aligned} dU &= 0 \\ d\tau &= 0 \end{aligned}$$

We can solve this by considering a reversible isothermal expansion of the gas. The work done on the gas in the reversible process from volume  $V_1$  to  $V_2$  is

$$W_{rev} = -N\tau \ln\left(\frac{V_2}{V_1}\right)$$

The work done on the gas is negative because the gas is doing work on the piston in order to expand. The heat transferred into the system is

$$\begin{aligned} Q_{rev} &= -W_{rev} > 0 \\ W_{rev} &< 0 \end{aligned}$$

In other words, gas draws the heat from the reservoir and uses it to do work on the piston. The associated entropy change is

$$\sigma_2 - \sigma_1 = -\frac{W_{rev}}{\tau} = N \ln\left(\frac{V_2}{V_1}\right)$$

Since in the irreversible expansion there is no work or heat transferred into the system,  $W_{irrev} = 0$ ,  $Q_{irrev} = 0$ . This gives us

$$\begin{aligned} W_{irrev} &> W_{rev} \\ Q_{irrev} &< Q_{rev} \end{aligned}$$

## Isothermal Work

The total work performed on a system in a reversible isothermal process is equal to the increase in the Helmholtz free energy  $F = U - \tau\sigma$  of the system.

$$dW = dU - dQ = dU - \tau d\sigma = dU - d(\tau\sigma) = dF$$

This means that in an isothermal process, the **Helmholtz free energy** is the most useful energy relation to use. The Helmholtz free energy automatically includes the additional work that is required to make up for the heat transfer from the system to the reservoir. In the case of some adiabatic process, such as an isothermal process of an ideal gas,  $dU = 0$  and the work done is equal to the heat transfer.

## Isobaric Heat and Work

If we consider a situation where an external atmospheric pressure is acting on a piston that is containing some boiling liquid, the work is  $-pdV = -d(pV)$ . If the work is positive, the environment is providing the work. If this work is negative, it is delivered to the environment and is not extractable from the system for other purposes. This leads us to an **effective work** performed on the system.

$$dW' = dW + d(pV) = dU + d(pV) - dQ = dH - dQ$$

This involves **enthalpy**  $H$  which plays the role in processes at constant pressure that the energy  $U$  plays in processes at constant volume and is defined as

$$H = U + pV$$

The  $pV$  in this expression is the work required to displace the surrounding atmosphere in order to vacate the space to be occupied by the system.

There are two special cases.

1. Processes where no effective work is done. This means  $dH = dQ$ . The evaporation of a liquid in an open container is an example.

2. Processes at constant temperature and constant pressure. This means  $dQ = \tau d\sigma = d(\tau\sigma)$  and the effective work is

$$dW' = dF + d(pV) = dG$$

where  $G$  is the **Gibbs free energy** and is defined by

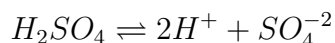
$$G = F + pV = U + pV - \tau\sigma$$

This is useful for chemical reactions where the volume changes as the reaction proceeds at constant pressure.

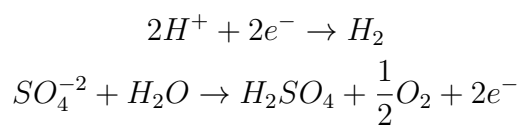


## Example: Electrolysis and Fuel Cells

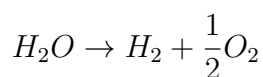
Electrolysis is an isobaric and isothermal process. Let's consider an electrolyte of dilute sulfuric acid in which are immersed inert platinum electrodes.



When a current is passed through the cell the hydrogen ions move to the negative electrode and the sulfate ions move to the positive electrode. The hydrogen ions take up electrons and form molecular hydrogen gas. The sulfate ions decompose water with the release of oxygen gas and electrons.



Combining these half reactions gives us



When carried out slowly with an open container, this process is isobaric and isothermal. The effective work is then

$$W' = \Delta G = G(H_2O) - G(H_2) - \frac{1}{2}G(O_2)$$

The Gibbs free energy difference  $\Delta G$  is -237 kJ/mol at room temperature.

The work is performed by a current  $I$  that flows under an external voltage  $V_0$ . If the time required to decompose a mole of water is  $t$ ,  $q = It$ , with  $q$  being the total charge flowing through the cell.

$$W' = qV_0$$

There are 2 electrons involved in decomposing one water molecule, so

$$q = -2N_A e = -1.93 \times 10^5 \text{coulomb}$$

The minimum voltage for this is then

$$V_0 = -\frac{\Delta G}{2N_A e} = 1.229 \text{volts}$$

With a voltage higher than this minimum, the excess power  $P = (V - V_0) \times I$  will be dissipated as heat in the electrolyte. With  $V < V_0$ , the reaction will proceed backwards if there is hydrogen gas available at the positive electrode and oxygen gas is available at the negative electrode. In an open container where the gases are able to escape, this backward reaction will not occur and nothing will happen. A fuel cell is an electrolysis cell operated in reverse. With  $V < V_0$  the cell is a fuel cell and when  $V > V_0$  the cell is an electrolysis cell.

## Chemical Work

When particles are able to transfer, the energy relation changes to

$$dU = \tau d\sigma - pdV + \mu dN$$

This gives us a new relation for the work.

$$dW = -pdV + \mu dN$$

The first term is what we've seen before as the mechanical work, and the second term is the chemical work. In particle transfer there is usually at least two systems, and the chemical work is the sum of the contributions from all systems.

Let's say we have particles leaving system 1  $\mathcal{S}_1$  and entering system 2  $\mathcal{S}_2$  with chemical potentials  $\mu_1$  and  $\mu_2$  respectively.  $dN = dN_2 = -dN_1$  is the number of particles transferred. The total chemical work is then

$$dW_c = dW_{c1} + dW_{c2} = \mu_1 dN_1 + \mu_2 dN_2 = (\mu_2 - \mu_1) dN$$

This gives us new ways to interpret the chemical potential:

1. The chemical potential of a system is the work required to transfer one particle into the system from a reservoir at zero chemical potential.
2. The difference in chemical potentials between two systems is equal to the net work required to move a particle from one system to the other.
3. If two systems are in diffusive equilibrium they have the same chemical potential and no work is required to move a particle from one system into the other.
4. The difference in internal chemical potential between two systems is equal but opposite to the potential barrier that maintains the systems in diffusive equilibrium.

## Example: Chemical Work for an Ideal Gas

We want to find the work per particle of moving a monatomic ideal gas from system  $\mathcal{S}_1$  with concentration  $n_1$  to system  $\mathcal{S}_2$  with concentration  $n_2$  when  $n_2 > n_1$ . Both systems begin at the same temperature and the volume is to remain constant. The difference in chemical potential is

$$\mu_2 - \mu_1 = \tau \left( \ln \left( \frac{n_2}{n_Q} \right) - \ln \left( \frac{n_1}{n_Q} \right) \right) = \tau \ln \left( \frac{n_2}{n_1} \right)$$

According to interpretation 2 of the chemical potential from the previous section, this difference in chemical potential must be equal to the net work, the mechanical work in this case,

to move a particle from  $\mathcal{S}_1$  to  $\mathcal{S}_2$ . The work required to compress  $N$  particles of an ideal gas from an initial volume  $V_1$  into a final volume of  $V_2$  is

$$W = - \int p dV = -N\tau \int \frac{dV}{V} = N\tau \ln\left(\frac{V_1}{V_2}\right) = N\tau \ln\left(\frac{n_2}{n_1}\right)$$

This shows that different types of work are convertible to each other.

## Magnetic Work and Superconductors

Many conductors below some critical temperature  $T_c$  transition from a state of finite conductivity to a superconducting state with almost infinite conductivity. The **Meissner effect** is the property of a superconductor to expel magnetic flux in their interior. It is caused by shielding currents that are spontaneously generated near the surface. Superconductors are considered type II if the expulsion is incomplete but nonzero.

A sufficiently strong magnetic field will destroy the superconducting phase. Superconductivity is a distinct thermodynamic phase. The heat capacity has a discontinuity at the onset of superconductivity  $\tau = \tau_c$ . If we look below this critical temperature with no magnetic field, the superconducting phase is the most stable. As the magnetic field is cranked up, the free energy of the superconducting phase increases until it eventually exceeds the free energy of the normal, non-superconducting phase, which is independent of applied magnetic field. When this happens, the normal, non-superconducting phase will be more stable and superconductivity is destroyed.

Consider a superconductor in the form of a long rod of uniform cross-section inside a long solenoid that produces a uniform field  $B$ . The work required to reduce the field to zero inside the superconductor is equal to the work required to create within the superconductor a counteracting field  $-B$  that cancels out the solenoid field. The work created from a  $B$  field is

$$\frac{W_{mag}}{V} = \frac{B^2}{2\mu_0} \Big|_{SI} = \frac{B^2}{8\pi} \Big|_{CGS}$$

When not in the superconducting phase, the free energy is no longer affected by a changing magnetic field so its free energy is

$$\frac{F_N(\tau) - F_S(\tau)}{V} = \frac{B_c^2(\tau)}{2\mu_0} \Big|_{SI} = \frac{B_c^2(\tau)}{8\pi} \Big|_{CGS}$$

With increasing temperature, the difference between the free energies between normal and superconducting phases shrinks until it reaches a critical temperature in which superconduction doesn't occur.