Foundations of Physics 2B - Summary

Thermodynamics

Heat Capacity

The heat capacity is defined by:

$$\delta Q = C \mathrm{d}T$$

Where δQ is the heat energy required to raise the temperature of a body by $\mathrm{d}T$.

The heat capacity at constant volume is:

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V = m c_V$$

Where m is the mass and c_V is the specific heat capacity at constant volume.

The same applies to constant pressure, C_P.

Zeroth Law of Thermodynamics

The zeroth law of thermodynamics states that if two thermodynamic systems are each in thermal equilibrium with a third one, then they are in thermal equilibrium with each other.

Partial Derivatives

The total differential of a function $z = f(x, y)$ is defined by:

$$\mathrm{d}z = \left(\frac{\partial f}{\partial x} \right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y} \right)_x \mathrm{d}y = M(x, y)\mathrm{d}x + N(x, y)\mathrm{d}y$$

If $f(x, y, z) = 9$ we know that $x = x(y, z)$ and $y = y(x, z)$. We then have two theorems:

Reciprocal theorem:

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z = 1$$

Reciprocity theorem or cyclic relation:

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1$$

Exact and Inexact Differentials

The total differential $\mathrm{d}z$ is exact if:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Which is true only if x and y are independent and so

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y}$$

This is equivalent to saying that:

$$I = \int_1^2 \mathrm{d}z(x,y) = \int_1^2 M(x,y)\mathrm{d}x + \int_1^2 N(x,y)\mathrm{d}y = z_2 - z_1$$

i.e. the integral of $\mathrm{d}z$ is *path independent*. All thermodynamic system properties (e.g. p, V, T, U, S) are such functions.

Note: Inexact differentials are denoted by δz.

First Law of Thermodynamics

If a system moves from an initial state, i, to a final state, f, via adiabatic paths, the work done is the same for all adiabatic paths.

Mathematically this can be stated as:

$$\mathrm{d}U = \delta Q + \delta W$$

Heat Capacity

Using the 1st Law, we find that:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Proof:

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V - \left(\frac{\partial W}{\partial T}\right)_V$$

However, at constant volume W is constant, so we get:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

We also find that:

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

Proof:

Using $\delta W = -p\mathrm{d}V$ we get:

$$\delta Q = \mathrm{d}U + p\mathrm{d}V$$

We can also find that for $U = U(T,V)$:

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$$

Combining the two gives:

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\mathrm{d}V$$

Using the definition of C_P:

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

Now, using the expression for C_V:

$$C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

And so:

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

For an ideal gas:

$$C_P - C_V = R$$

We can also define the adiabatic index as:

$$\gamma = \frac{C_P}{C_V}$$

Reversible and Irreversible Processes

A process is reversible if:

- No frictional or dissipative forces exist
- No heat conduction is present due to finite temperature differences
- The process is quasi-static

Adiabatic and Diathermal Walls

An adiabatic wall means no heat can be exchanged through it whilst a diathermal wall does allow the passage of heat.

The equation of state for an ideal gas under adiabatic conditions is:

$$pV^\gamma = \text{constant}$$

Heat Engines

Heat engines are machines that produce work using a temperature difference between two heat reservoirs, known as a heat source and a heat sink.

Efficiency of a Heat Engine

In general:

$$\text{Efficiency} = \eta = \frac{\text{Product}}{\text{Expense}}$$

For a heat engine:

$$\eta = \frac{|\text{Work Done}|}{\text{Heat Input}} = \frac{Q_H - Q_L}{Q_H}$$

For a fridge:

$$\text{COP}_L = \frac{\text{Heat from Cold Reservoir}}{\text{Work Supplied}} = \frac{Q_L}{W}$$

For a heat pump:

$$\text{COP}_H = \frac{\text{Heat to Hot Reservoir}}{\text{Work Supplied}} = \frac{|Q_H|}{W}$$

Second Law of Thermodynamics

Clausius Statement:

It is impossible to devise a process whose sole result is the transfer of heat from a cold to a hot reservoir.

Kelvin-Planck Statement:

It is impossible to construct a device that operates in a cycle producing positive work that only interacts with one heat reservoir.

These two laws are logically equivalent.

More on Reversibility

- To show a process is reversible it is sufficient to show a reversible process exists
- To show a process is irreversible, it is sufficient to show that it violates the second law
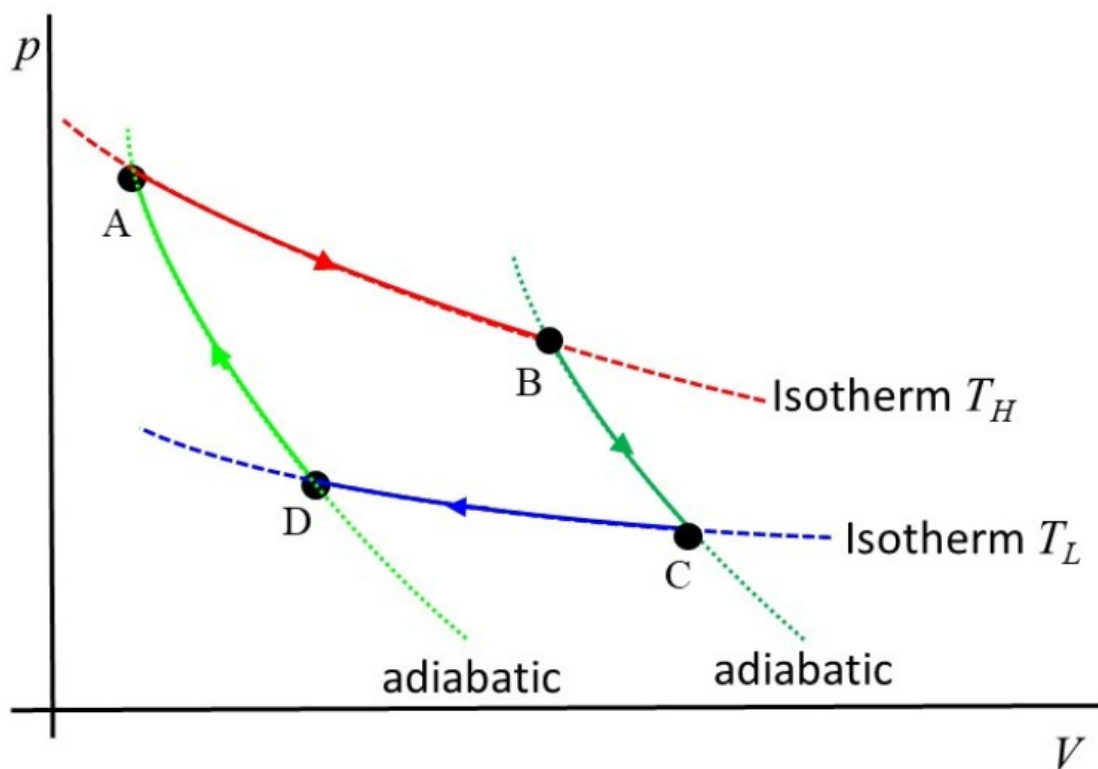
Carnot Engines

Figure 9: pV diagram for a Carnot Cycle.

The Carnot cycle is reversible.

We find the following relationship from the cycle:

$$\frac{Q_H}{|Q_L|} = \frac{T_H}{T_L}$$

This allows us to write the following as:

$$\eta = 1 - \frac{T_L}{T_H}; \quad \text{COP}_L = \frac{T_L}{T_H - T_L}; \quad \text{COP}_H = \frac{T_H}{T_H - T_L}$$

Proof of the Carnot Relation:

Work done on the isotherms at temperatures T_H ($-\delta W_{AB} = \delta Q_{AB}$) and T_C respectively are:

$$Q_H = -\int_A^B -pdV = \int_{V_A}^{V_B} \frac{RT_H}{V} dV = RT_H \ln\left(\frac{V_B}{V_A}\right)$$

$$Q_L = -\int_C^D -pdV = RT_L \ln\left(\frac{V_D}{V_C}\right) = -RT_L \ln\left(\frac{V_C}{V_D}\right)$$

The ratio of the heats is therefore given by:

$$\frac{Q_H}{|Q_L|} = \frac{T_H}{T_L} \frac{\ln(V_B/V_A)}{\ln(V_C/V_D)} \qquad (*)$$

Using the equation of state for an ideal gas under adiabatic conditions:

$$p_A V_A^\gamma = p_D V_D^\gamma; \quad p_B V_B^\gamma = p_C V_C^\gamma$$

Since $pV = RT$, we can eliminate the pressures in terms of temperature:

$$p_A V_A = RT_H = p_B V_B; \quad p_C V_C = RT_L = p_D V_D$$

Hence

$$RT_H V_B^{\gamma-1} = RT_L V_C^{\gamma-1}; \quad RT_H V_A^{\gamma-1} = RT_L V_D^{\gamma-1}$$

And so:

$$\frac{T_H}{T_L} = \left(\frac{V_C}{V_B}\right)^{\gamma-1} \equiv \left(\frac{V_D}{V_A}\right)^{\gamma-1}$$

Which gives:

$$\frac{V_C}{V_D} = \frac{V_B}{V_A}$$

Substituting this into (*) gives us the Carnot Relation:

$$\frac{Q_H}{|Q_L|} = \frac{T_H}{T_L}$$

Carnot Principles

There are two Carnot Principles:

- *Of all the heat engines working between two temperatures, none is more efficient than a Carnot engine.*
- *All reversible heat engines operating between two heat reservoirs have the same efficiency.*
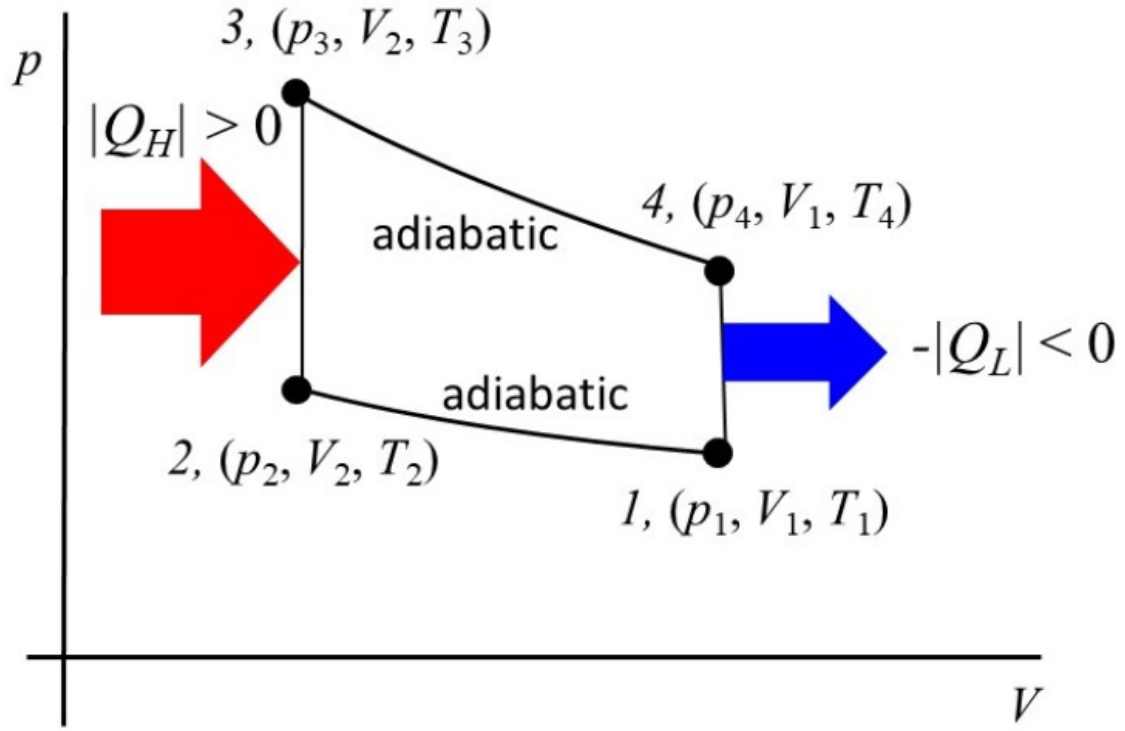
Otto Cycle

Figure 14: pV diagram of ideal Otto cycle.

The efficiency of an Otto cycle (for petrol engines) is given by:

$$\eta_{\text{Otto}} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \left(\frac{V_1}{V_2}\right)^{1-\gamma} = 1 - r^{1-\gamma}$$

Where r is the compression ratio which is typically between 7 and 10.

Proof:

Considering each process for the Otto cycle in turn:

1 to 2: An adiabatic compression with

$$p_1 V_1^\gamma = p_2 V_2^\gamma \quad \Rightarrow \quad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

2 to 3: Isothermal heating with

$$Q_H = \int_{T_2}^{T_3} C_V \, dT = C_V (T_3 - T_2) > 0$$

3 to 4: Adiabatic expansion with

$$p_3 V_3^\gamma = p_4 V_4^\gamma \quad \Rightarrow \quad T_3 V_3^{\gamma-1} = T_4 V_4^{\gamma-1} \quad \Rightarrow \quad T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$$

4 to 1: Isothermal cooling with:

$$Q_L = \int_{T_4}^{T_1} C_V \, dT = C_V (T_1 - T_4) < 0$$

The efficiency is hence:

$$\eta = 1 - \frac{|Q_L|}{Q_H} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

Considering the adiabatic parts, we can write:

$$T_1 = \frac{T_2 V_2^{\gamma-1}}{V_1^{\gamma-1}}$$

And:

$$\frac{T_3 V_2^{\gamma-1}}{T_4^{\gamma-1}} = V_1^{\gamma-1}$$

Which gives:

$$\frac{T_1}{T_4} = \frac{T_2}{T_3}$$

Rearranging the efficiency gives:

$$\eta = 1 - \frac{T_1 \left[\left(\frac{T_4}{T_1} \right) - 1 \right]}{T_2 \left[\left(\frac{T_3}{T_2} \right) - 1 \right]}$$

Since the two terms in brackets are equal, we can write the efficiency as:

$$\eta_{\text{Otto}} = 1 - \left(\frac{V_1}{V_2} \right)^{1-\gamma} = 1 - r^{1-\gamma}$$
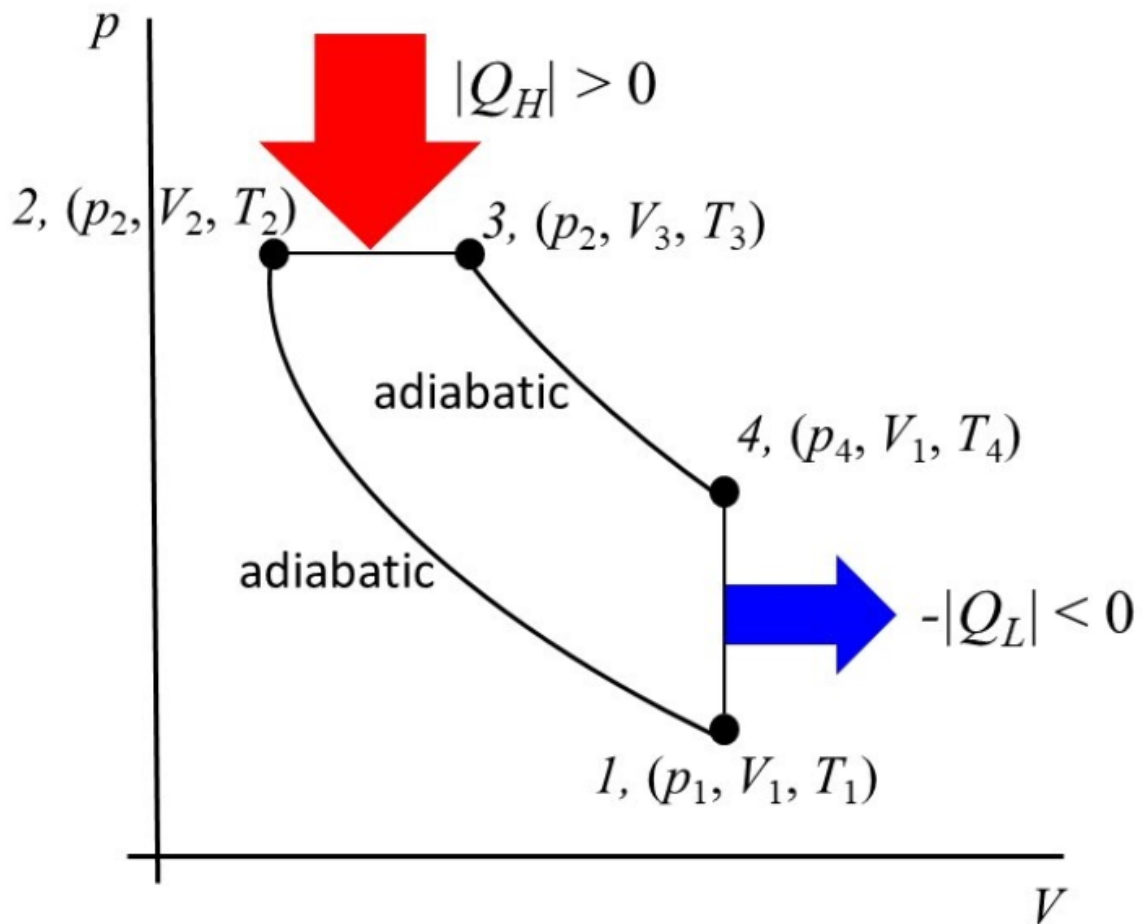
Diesel Cycle

Figure 16: pV diagram of ideal Diesel Cycle.

The efficiency of the Diesel cycle (for diesel engines) is given by:

$$\eta_{\text{Diesel}} = 1 - \frac{1}{r^{\gamma-1}} \left[\frac{(r_c^\gamma - 1)}{\gamma(r_c - 1)} \right]$$

Where $r_c = V_3/V_2$ is the cut-off ratio. In the limit that $r_c \to 1$ the efficiency becomes the same as the Otto cycle.
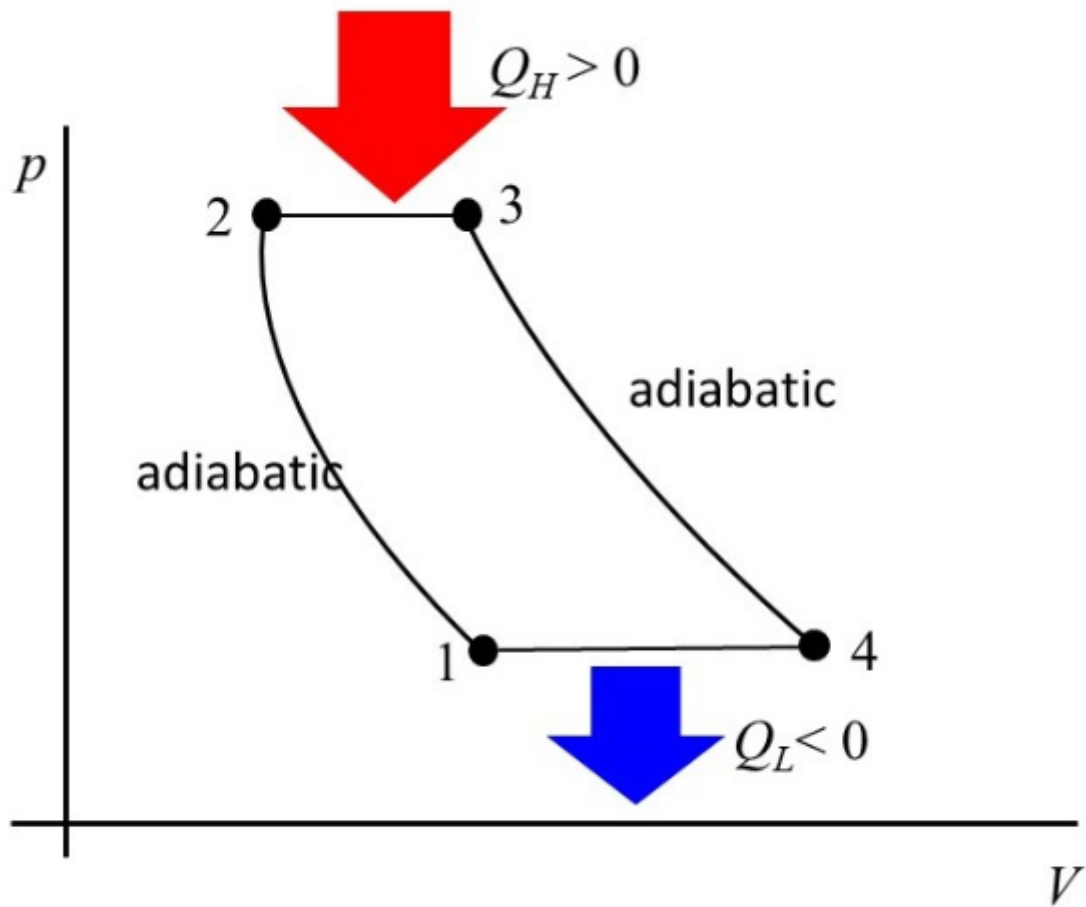
Brayton Cycle

Figure 20: Brayton cycle pV diagram.

The efficiency of the Brayton cycle (for gas turbines) is:

$$\eta_{\text{Brayton}} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = \frac{1}{r_p^{(\gamma-1)/\gamma}}$$

Where $r_p = p_2/p_1$ is the pressure ratio.

Clausius Inequality

The Clausius inequality tells us that:

$$\oint \frac{\delta Q}{T} \leq 0$$

Heat is thus not conserved in a thermodynamic process, unless it is reversible and places a direction on some processes.

Entropy

The entropy change between two thermodynamic states, A and B, is

$$\mathrm{d}S = \frac{\delta Q_{\text{rev}}}{T}$$

So

$$S(B) - S(A) = \int dS = \int_A^B \frac{\delta Q}{T}$$

An adiabatic process has no heat change ($\delta Q = 0$) and so known as an *isentropic process*.

Entropy Change for any Process

The entropy change for an irreversible process is:

$$\Delta S = \int_A^B \frac{\delta Q_{\text{rev}}}{T} \geq \int_A^B \frac{\delta Q}{T}$$

Where δQ_{rev} is the reversible heat energy change.

Hence we find that:

$$\delta Q \leq T dS$$

And since $\delta Q = 0$ in thermally isolated systems:

$$dS \geq 0$$

Entropic Statement of the Second Law

In every process taking place in an ideal system, the entropy change of the system either increases or remains constant.

First Law in Terms of Entropy

The first law of thermodynamics can be written as:

$$dU = T dS - p dV$$

Internal Energy

The function of state U has natural variables of S and V, so we can write $U = U(S, V)$. Since dU is an exact differential, we can always write $dU = U_f - U_i$.

We can also write for a reversible isochoric process:

$$\Delta U = \int_{T_1}^{T_2} C_V dT$$

Enthalpy

A similar relationship at constant pressure is enthalpy which is defined as:

$$H = U + pV$$

Hence:

$$dH = T dS + V dp$$

Enthalpy as natural variables S and p, with $H = H(S, p)$ and represents the heat absorbed by the system at constant pressure:

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

Helmholtz Function

The Helmholtz function is termed a free energy and is defined as:

$$F = U - TS$$

And hence:

$$\mathrm{d}F = -p\mathrm{d}V - S\mathrm{d}T$$

It has natural variables V and T, with $F = F(V, T)$. For a reversible, isothermal process $\mathrm{d}F = -p\mathrm{d}V$.

Gibbs Function

Another free energy, it is defined as:

$$G = H - TS = F + pV = U + pV - TS$$

Hence:

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$$

With natural variables p and T, so $G = G(p, T)$. G represents the maximum mechanical work that can be done between equilibrium states and is conserved in isothermal, isobaric process (e.g. at a phase transition).

Maxwell Relations

The four relationships are:

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

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_S$$

$$T = -\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p$$

$$V = \left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T$$

These can then be manipulated to find the Maxwell Relations:

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \tag{M1}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{M2}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{M3}$$

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \tag{M4}$$

Generalised Quantities

The general form of the heat capacity at some constant property, α, is:

$$C_\alpha = \left(\frac{\partial Q}{\partial T}\right)_\alpha = T\left(\frac{\partial S}{\partial T}\right)_\alpha$$

Generalised susceptibilities quantify how much something changes when a generalised force is applied. Common ones are the isobaric and adiabatic expansivities:

$$\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p; \quad \beta_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S$$

Similarly the isothermal and adiabatic compressibilities give the fractional volume changes when pressure is applied and are defined by:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T; \quad \kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$$

$T\mathrm{d}S$ and Energy Equations

The $T\mathrm{d}S$ equations are:

$$T\mathrm{d}S = C_V\,\mathrm{d}T + T\left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V \tag{TS1}$$

$$T\mathrm{d}S = C_p\,\mathrm{d}T - T\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p \tag{TS2}$$

The energy equations are:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{E1}$$

$$\left(\frac{\partial U}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial p}\right)_T \tag{E2}$$

Effectiveness of a Process

The effectiveness of a process is defined as:

$$\text{Effectiveness} = \eta_{\text{rev}} = \frac{|\text{Best Possible Work}|}{\text{Heat In}}$$

The Second Law Efficiency is then:

$$\eta_{2\text{nd}} = \frac{\text{Actual Efficiency}}{\text{Effectiveness}}$$

Availability and Available Energy

The available energy of a device (also known as the device's exergy) tells us the maximum work that could be obtained from a system in a particular state, operating in a specific environment.

The available work and availability are defined via the following, where p_0 and T_0 are the pressure and temperature of the environment:

$$A = U + p_0 V - T_0 S$$

$$\mathrm{d}A = \mathrm{d}U + p_0\left(V_2 - V_1\right) - T_0\left(S_2 - S_1\right)$$

Relationship to Thermodynamic Potentials

If the Helmholtz function is considered, we can find that:

$$\delta W \geq \mathrm{d}F$$

With the equality holding in reversible processes.

At thermal equilibrium, the Helmholtz function takes a minimum value.

Useful Work and Irreversibility

The useful work is defined as the difference between the actual work done during the thermodynamic process (total work produced by the device) and the surroundings work (which would be done against the atmosphere, or is dissipated as heat etc.):

$$W_{\text{use}} = W_{\text{act}} - W_{\text{surr}}; \quad W_{\text{surr}} = p_0(V_2 - V_1)$$

The reversible work, W_{rev} is defined as the maximum amount of useful work that can be produced by a device, or minimum work that must be supplied to a system, as it undergoes a change between two states, when operating on a reversible cycle.

The irreversibility of a process is defined as:

$$I = W_{\text{rev}} - W_{\text{use}} = T_0 \Delta S_{\text{Universe}}$$

Where T_0 is the Universe temperature (normally that of the external environment) and $\Delta S_{\text{Universe}}$ is the change of the entropy of the universe.

Latent Heats

The latent heat of a phase change is:

$$L = \Delta Q_{\text{rev}} = T_0 \Delta S$$

In other words, at a phase change the entropy changes from $S_1 \to S_2$ at constant temperature T_0.

Clausius-Clapeyron Equation

This equation describes how pressure changes with temperature for a system having two phases which are in equilibrium:

$$\left(\frac{\partial p}{\partial T} \right)_{i \to f} = \frac{L_{i \to f}}{T(V_f - V_i)}$$

Where $L_{i \to f}$ is the specific heat of transformation on going from phase i to phase f.

Joule-Kelvin Effect

For a gas expanding through a porous plug at constant enthalpy, we can define the Joule-Kelvin coefficient, a measure of how the temperature changes with respect to the pressure, as:

$$\mu_{\text{JK}} = \left(\frac{\partial T}{\partial p} \right)_H = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right]$$

Third Law of Thermodynamics

Nernst's statement:

The entropy change of any reaction in a system in internal equilibrium is zero near absolute zero.

Planck's statement:

The entropy change of all systems in internal equilibrium is the same at absolute zero, and may be taken to be zero.

Third Law Consequences

The contribution to the entropy of a system by each aspect of the system which is in thermodynamic internal equilibrium tends to zero as $T \to 0$.

It is impossible to reach $T = 0$ in a finite number of steps.

Thermodynamics of Real Gases

The van der Waals equation is given by:

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

Condensed Matter Physics