PY2005: Thermodynamics

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These notes cover the Senior Freshman course given by
Dr. Graham Cross in Michaelmas Term 2007, except
for lecture 12 on phase changes.

Some Multivariate Calculus

Functions relating (for example) pressure, volume and temperature occur frequently in thermo-
dynamics. Hence we need some results from the calculus of many variables.

Consider a function $F(x, y, z) = 0$, where $x = x(y, z)$ and $y = y(x, z)$, then

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

and subbing the latter into the former gives

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz$$

Now let x, z be independent. Then for $dz = 0$, dx is arbitrary, so

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

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

the inverse relation.

Now let $dx = 0$, so

$$0 = \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz$$

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

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

the cyclical relation.

Finally, consider a function $f(x, y)$. In differential form

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

As this is the differential of a mathematical function, this is known as an exact differential. For such functions we have $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$. Now consider some arbitrary differential

$$df = X(x,y)dx + Y(x,y)dy$$

A necessary and sufficient condition for df to be exact is then

$$\left(\frac{\partial X}{\partial y}\right)_x = \left(\frac{\partial Y}{\partial x}\right)_y$$

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

Temperature

We begin our study of thermodynamics with some basic definitions that lead us to the idea of temperature.

Definition: (System, Surroundings, Boundary) In our study of thermodynamics we concern ourselves with a particular part of the universe we will call a *system*. The rest of the universe is known as the *surroundings*, separated by a *boundary* which may allow the exchange of energy and matter. We shall restrict ourselves to the study of *closed systems*, in which only energy may be transferred.

Definition: (Equilibrium State, State Variables) An *equilibrium state* is one in which all the bulk physical properties of the system are uniform throughout the system and do not change with time. An equilibrium state is specified by two independent variables known as *state variables*.

Definition: (Thermal Equilibrium) If two thermodynamic systems are left in thermal contact with each other, and after some time the two systems are in an equilibrium state with no further changes occurring, then the systems are said to be in *thermal equilibrium* with each other.

Law: (Zeroth Law Of Thermodynamics) If each of two thermodynamic systems are in thermal equilibrium with a third, they are in thermal equilibrium with each other.

Definition: (Temperature) The *temperature* of a system is a property that determines whether or not that system is in thermal equilibrium with other systems.

Definition: (Equations of State) An *equation of state* of a system is a relationship between the two independent state variables and the temperature, of the form $f(X, Y, T) = 0$ where X and Y are the two state variables.

    e.g. for an ideal gas, the equilibrium state is described by the independent variables P and V (pressure and volume), using the ideal gas equation

$$PV = nRT$$

Temperature Scales: We measure temperature using thermometric properties of a system. These are measurable properties that vary with temperature, eg as $X = cT_X$ where X is the thermometric property, c is a constant and T_X is the temperature as measured using X. We fix c by choosing some fixed and easily reproducible point T_X and assigning to it a particular value.

e.g. the conventional choice is the triple point of water, which is assigned $T_{tp} = 273.16$, and then $c = \frac{X_{tp}}{273.16}$, giving the following expression for temperature as:

$$T_X = 273.16 \frac{X}{X_{tp}}$$

Note that this implies a zero of temperature on the X scale, which may not actually occur owing to the particular properties of X. Also, the use of this formula for temperature is limited by X being practically measurable.

Of particular interest is the gas scale, which uses the pressure of a gas as the thermometric property X. As the quantity of gas used goes to zero, it is found that all gases give the same value for temperature of a given system. We thus define the gas scale:

$$T = 273.16 \lim_{P_{tp} \to 0} \frac{P}{P_{tp}} K$$

where K, or kelvin, is the unit of temperature. The constant 273.16 was chosen so as to ensure there were exactly 100K between the melting and boiling points of water.

Work

In thermodynamics we are interested in the changes in state functions that occur when a system changes from one equilibrium state to another, and the work done by or on the system during these changes.

Definition: (Process) A *process* is the method or mechanism by which a system changes from one equilibrium state to another.

Definition: (Quasistatic Process) A *quasistatic process* is a process which is a succession of equilibrium states.

Definition: (Reversible Process) A *reversible process* is a quasistatic process where no dissipative forces are present.

Example: (Reversible and Irreversible) Consider the standard gas and piston system:
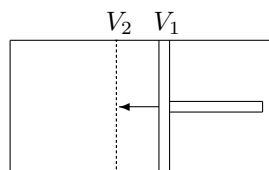
If we move the piston in slowly, such that the changes in volume from V_1 to V_2 are infinitesimal, then the equation of state $PV = nRT$ holds at every point during the process - hence it is reversible. If we suddenly push the piston from V_1 to V_2 turbulence and temperature gradients are set up, and the process is irreversible even though the end points (P_1, V_1) and (P_2, V_2) are the same as before.

Sign Convention for Work: When the surroundings do work on the system, the work is positive. When the system does work on its surroundings the work is negative.

Example: (Work) Consider the same system as in the previous example, and the effect of moving the piston a distance dx outwards. The force on the gas is $F = PA$ (with A being area of the piston's face), and the work done is

$$dW = -PA\,dx = -P\,dV$$

$$\Rightarrow W = -\int_{V_1}^{V_2} P\,dV$$

Note that work is path dependent, and hence is an inexact differential. We write it in infinitesimal form as $\dbar W$.

Definition: (Intensive and Extensive Variables) An intensive variable is size independent (e.g. pressure, force). An extensive variable is size dependent (e.g. volume, length). The expression for work always involves one of each kind, that is: $\dbar W =$ intensive d(extensive).

Definition: (Configuration Work) For reversible processes we have $\dbar W = Y_1 dX_1 + Y_2 dX_2 \ldots$ - for intensive variable Y_i and extensive variable X_i. This is known as the *configuration work*. $(X_1, X_2 \ldots)$ is known as the *system configuration*.

Irreversible processes cannot be expressed in terms of states variables (usually - in some special cases irreversible processes do allow for work to be defined using sate variables). We instead have (say) $\dbar W = -PdV +$ dissipative work. This leads to:

$$\text{Total Work} = \text{Configuration Work} + \text{Dissipative Work}$$

Heat

The First Law of Thermodynamics relates work, heat and internal energy. It was discovered empirically, on the basis of experiments by Joule who found that the amount of work needed to raise the temperature of a thermally isolated system was independent of how the work was carried out.

Definition: (Adiabatic Process) An *adiabatic process* is one in which the temperature of the system is independent of the surroundings (i.e. the system is thermally isolated).

Law: (First Law Of Thermodynamics) If a thermally isolated system is brought from one equilibrium state to another (i.e. in an adiabatic process), the work necessary to achieve this change is independent of the process used.

Definition: (Internal Energy) Adiabatic work is path and process independent, and depends only on the endpoints of a system in equilibrium, implying the existence of a state function U of the system such that $W_{adiabatic} = U_2 - U_1$. This U is called the *internal energy* of the system.

Law: (First Law Of Thermodynamics) For forms of work other than adiabatic work, it is clear that $W \neq W_{adiabatic} = U_2 - U_1$. So that energy is conserved, some other energy exchange must take place - this exchange is the flow of heat into or out of the system, and leads to the mathematical statement of the First Law:

$$\Delta U = W + Q$$

or infinitesimally,

$$dU = \dbar W + \dbar Q$$

Definition: (Heat) *Heat* is the non-mechanical exchange of energy between the system and the surroundings, denoted by Q or infinitesimally as $đQ$.

Sign Convention for Heat: The heat Q is positive for heat entering the system, and negative for heat leaving the system.

Definition: (Heat Capacity) Consider a reversible flow of heat Q into a system, with a corresponding temperature change ΔT. We define the *heat capacity* C to be:

$$C = \lim_{\Delta T \to 0} \frac{Q}{\Delta T} = \frac{đQ}{dT}$$

This is an extrinsic property of the system. We can define an intrinsic version known as the *specific heat capacity* as

$$c = \frac{1}{m} \frac{đQ}{dT}$$

where m is the mass of the system. Note that the expression $\frac{đQ}{dT}$ should not be considered a derivative, and also that heat capacity is path dependent.

Example: (Heat Capacity at Constant Volume for Ideal Gas) For an ideal gas and from the first law we have $dU = -PdV + đQ$, but here $dV = 0$, hence $dU = đQ$. This gives us our definition for heat capacity at constant volume:

$$C_V = \lim_{\Delta T \to 0} \frac{Q}{\Delta T} = \frac{đQ}{dT} = \left(\frac{\partial U}{\partial T} \right)_V$$

Definition: (Enthalpy) The *enthalpy* H is defined as:

$$H = U + PV$$

Example: (Heat Capacity at Constant Pressure for Ideal Gas) Consider the enthalpy H, then $dH = dU + PdV + VdP$. Subbing in for dU from the first law, we get $dH = đQ + VdP$, and for a constant pressure process $dH = đQ$. Hence the heat capacity at constant pressure is:

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

Difference of Heat Capacities, Ideal Gas: From the first law

$$dU = đW + đQ$$

$$\Rightarrow đQ = C_v dT + PdV$$

and then differentiating with respect to T at constant pressure:

$$\left(\frac{đQ}{dT} \right)_P = C_p = C_v + P \left(\frac{\partial V}{\partial T} \right)_P$$

$$\Rightarrow C_p = C_v + nR$$

using the ideal gas law.

Adiabatic Gas Expansion: From the first law

$$đQ = 0 = dU + PdV$$

$$\Rightarrow 0 = C_v dT + PdV$$

$$\Rightarrow \int C_v \frac{dT}{T} = -nR \int \frac{dV}{V}$$

using the ideal gas law. Integrating gives:

$$C_v \ln T = -nR \ln V + \text{constant}$$

$$\Rightarrow \ln T = -\frac{C_p - C_v}{C_v} \ln V + \text{constant}$$

and we define the ratio of heat capacities to be $\gamma = \frac{C_p}{C_v} > 1$, so

$$\ln T = -(\gamma - 1) \ln V + \text{constant}$$

$$\Rightarrow T = \text{constant} \times V^{1-\gamma}$$

So for an adiabatic gas expansion

$$TV^{\gamma-1} = \text{constant}$$

and

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

Engines

Early study of thermodynamics was a result of the development of the steam engine and the need to understand and improve their operation.

Definition: (Heat Engine) A *heat engine* is a device that in general:

1. Receives heat Q_2 at a high temperature

2. Does some mechanical work on its surroundings

3. Rejects heat Q_1 at a lower temperature

 The net heat flow is then

$$Q = Q_2 - Q_1$$

A *cyclic heat engine* is a heat engine that operates in a cycle. We then have:

$$\Delta U = 0 = -W + Q$$

$$\Rightarrow W = Q$$

with the minus sign due the fact that the system is doing work on the surroundings.

Definition: (Thermal Efficiency of Heat Engine) The *thermal efficiency* of a heat engine is defined as the ratio of output work to input heat:

$$\eta = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} = 1 - \frac{Q_1}{Q_2}$$

Carnot Cycle: Any cyclic process bounded by two isotherms and two adiabatics is a Carnot cycle. Consider such a process, ABCDA. It operates as a heat engine as follows:

- $A \to B$: reversible isothermal process. The system does work W_2 and heat Q_2 flows in, at temperature T_2.

- $B \to C$: reversible adiabatic process. The system cools from T_2 to T_1, and does work W'.

- $C \to D$: reversible isothermal process. The system does work W_1 and heat Q_1 flows out, at temperature T_1.

- $D \to A$: reversible adiabatic process. The system warms from T_1 to T_2, and does work W''.

Example: (Carnot Cycle for Ideal Gas) Consider first the isotherms:

- $A \to B$: $\Delta U = 0 = W_2 + Q_2$

$$\Rightarrow Q_2 = -\left(- \int_A^B P dV \right) = nRT_2 \int_A^B \frac{dV}{V} = nRT_2 \ln\left(\frac{V_B}{V_A} \right)$$

- $C \to D$: Similarly,

$$Q_1 = -W_1 = nRT_1 \ln\left(\frac{V_C}{V_D} \right)$$

In the first case the system does work and gains heat, while in the second it is worked on and loses heat.

In the case of the adiabatic parts of the cycle, we have $TV^{\gamma-1} =$ constant, so:

$$T_2 V_B^{\gamma-1} = T_1 V_C^{\gamma-1}$$

$$T_2 V_A^{\gamma-1} = T_1 V_D^{\gamma-1}$$

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

$$\Rightarrow \frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

Hence,

$$\eta = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$$

Definition: (Coefficient of Performance for Carnot Refrigerator) For a *Carnot refrigerator* (just a Carnot cycle performed in the opposite direction) we have the *coefficient of performance* c defined as the ratio of extracted heat to input work:

$$c = \frac{Q_1}{W} = \frac{Q_1}{Q_2 - Q_1}$$

Second Law Of Thermodynamics

The Second Law of Thermodynamics imposes limits on the behaviour and efficiency of heat engines.

Law: (Second Law of Thermodynamics) It is impossible to construct a device that, operating in a cycle, will produce no effect other than the extraction of heat from a single body at a uniform temperature and the performance of an equivalent amount of work. (Kelvin-Plank)
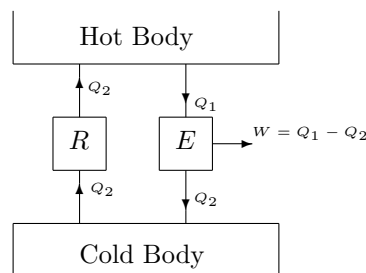
or equivalently,

It is impossible to construct a device that, operating in a cycle, produces no effect other than the transfer of heat from a colder to a hotter body. (Clausius)

Proof of Equivalence of the Kelvin-Plank and Clausius statements: Suppose the Kelvin-Plank statement untrue. Then it is possible to have an engine E which takes heat Q_1 from a hot body and delivers work $W = Q_1$. Let this engine drive a refrigerator R (such that W is sufficient to drive one cycle of R), which extracts heat Q_2 from a cold body.
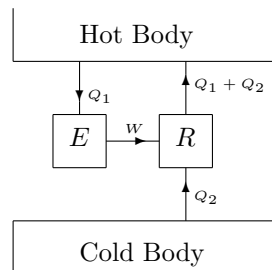
The composite system $E + R$ then takes heat Q_2 from the cold body and delivers heat $Q_2 + Q_1 - Q_1 = Q_2$ to the hot body, thus violating the Clausius statement of the second law.

Now suppose the Clausius statement untrue. Then we can have a refrigerator R which extracts heat Q_2 from a cold body and delivers the same heat Q_2 to a hot body in one cycle. Let us then construct an engine E operating between the two bodies such that in one cycle it extracts heat Q_1 from the hot body, and delivers heat Q_2 to the cold body, doing work $W = Q_1 - Q_2$.

The composite system $E + R$ then takes heat $Q_1 - Q_2$ from the hot body, and delivers the same amount of work, thus violating the Kelvin-Plank statement of the Second Law. Hence the two statements are equivalent.

Carnot's Theorem: No engine operating between two reservoirs can be more efficient than a Carnot engine operating between those two reservoirs.

To prove Carnot's theorem, suppose that there exists an engine E' with efficiency $\eta' > \eta_c$. This engine extracts heat Q'_1 from the hot reservoir, performs work W' and delivers heat $Q'_2 = Q'_1 - W'$ to the cold reservoir. Let us also have a Carnot engine C, efficiency η_c, between the two reservoirs, performing the same amount of work and delivering heat $Q_2 = Q_1 - W$ to the cold reservoir.
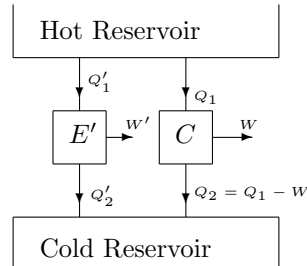
If $\eta' > \eta_c$, then

$$\frac{W'}{Q'_1} > \frac{W}{Q_1}$$

$$\Rightarrow Q_1 > Q'_1$$

as $W = W'$. Now, we can also drive the Carnot engine backwards as a refrigerator, extracting heat $Q_2 = Q_1 - W$ from the cold reservoir and delivering heat Q_1 to the hot reservoir. This acts with the engine E' as a composite system shown below:
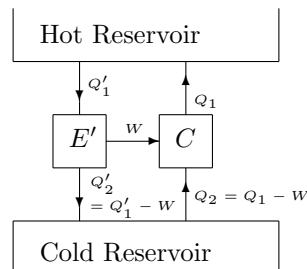
The composite system $E' + C$ extracts positive heat $Q_1 - Q'_1$ from the cold reservoir and delivers the same heat to the hot reservoir, with no external work required. This violates the Clausius statement of the Second Law, and implies that our assumption $\eta' > \eta_c$ is incorrect. Hence,

$$\eta \leq \eta_C$$

with equality if $Q'_1 = Q_1$.

Corollary to Carnot's Theorem: All Carnot engines operating between the same two reservoirs have the same efficiency.

This is proved using a similar argument to before, and letting each of the Carnot engines drive the other backwards as a refrigerator, to show that $\eta'_c \leq \eta_c$ and $\eta_c \leq \eta'_c$, proving that $\eta_c = \eta'_c$.

Entropy

One of the most important concepts in thermodynamics is that of entropy.

Definition: (Thermodynamic Temperature) For any material, we can define an *absolute temperature* by:
$$\frac{|Q_2|}{|Q_1|} = \frac{T_2}{T_1}$$
where $T = A\,\phi(\theta)$, with A being some constant of proportionality and $\phi(\theta)$ being some function, possibly unknown, of a thermometric property θ.

Clausius Inequality: Consider some cyclic process, acting on a working substance whose state is unchanged at the end of the cycle, and suppose its initial temperature is T_1. We consider the changes to the substance being ultimately due to a principal external reservoir at $\widetilde{T}$, and consider the process as being composed of many small Carnot cycles operating between auxillary reservoirs at $\widetilde{T}$ and the substance at temperatures T_i. For instance, a Carnot cycle operates between an auxillary reservoir at $\widetilde{T}$ and the substance at T_1 to raise the temperature to T_2, by supplying heat δQ_1. This takes heat $\frac{\widetilde{T}}{T_1}\delta Q_1$ from the $\widetilde{T}$ reservoir (from the definition of absolute temperature) and does work δW_1.

For the entire process, we have $dU = 0$, $Q = \sum_i \frac{\widetilde{T}}{T_i}\delta Q_i$ and $W = \sum_i \delta W_i$. From the first law,
$$0 = Q - W \Rightarrow W = Q$$

and the composite system of all the auxillary reservoirs has the effect of extracting heat from just one reservoir (the principal external one) and performing an equivalent amount of work. This violates the Second Law, unless both W and Q are negative (work is done on the system and the same quantity of heat flows out) or zero. Hence we have that

$$W = Q \leq 0$$

or

$$\widetilde{T}\sum_i \frac{\delta Q_i}{T_i} \leq 0$$

and in the infinitesimal limit,

$$\oint \frac{đQ}{T} \leq 0$$

which is the *Clausius inequality*. Equality holds in the reversible case (as in that case we could take our cycle in the opposite direction to obtain the reverse form of the inequality).

Entropy: In a reversible process, we have $\oint \frac{đQ_r}{T} = 0$, hence the integral $\int \frac{đQ_r}{T}$ is path independent. It follows that there must be a state function S such that

$$\Delta S = S_b - S_a = \int_a^b \frac{đQ_r}{T}$$

We call S the *entropy*, defined by:

$$dS = \frac{đQ_r}{T}$$

Principle of Increasing Entropy: Consider some cyclic process consisting of an irreversible

path from a to b followed by a reversible path from b to a again. We have

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

$$\Rightarrow \int_a^b \frac{\dj Q}{T} + \int_b^a \frac{\dj Q_r}{T} \leq 0$$

$$\Rightarrow \int_a^b \frac{\dj Q}{T} \leq -\int_b^a \frac{\dj Q_r}{T} = \int_a^b \frac{\dj Q_r}{T} = S_b - S_a = \Delta S$$

So for an infinitesimal part of a process

$$\frac{\dj Q}{T} \leq dS$$

with equality if the process is reversible. Hence in an infinitesimal irreversible process there is a definite entropy change dS. If the system is thermally isolated then $\dj Q = 0$. Hence

$$dS \geq 0$$

So for an isolated system, the entropy either increases or remains constant. It follows that an isolated system has maximum entropy when in equilibrium. The entropy of a non-isolated system can decrease, but it is always found that the entropy of the surroundings increase by at least the same amount.

Example: (Entropy in Different Processes)

- Reversible adiabatic processes: $\dj Q = 0$ and so $dS = 0$. Hence these are isentropic processes.

- Reversible isothermal processes:

$$\Delta S = S_b - S_a = \int_a^b dS = \int_a^b \frac{\dj Q_r}{T} = \frac{1}{T} \int_a^b \dj Q_r = \frac{Q_r}{T}$$

- Carnot cycle:

$$\int_A^B T dS = \int_A^B T \frac{\dj Q_2}{T} = \int_A^B \dj Q_2 = Q_2$$

so

$$\oint T dS = Q_2 - Q_1 = Q$$

On a T-S diagram, a Carnot cycle takes the shape of a rectangle.

- Irreversible processes: Since entropy is a state function, changes to it only depend on the end points. Hence, to calculate the entropy change due to an irreversible process, we can instead construct a reversible process with the same end points, and use it to work out the entropy change.

e.g. Irreversible heat flow from large reservoir at temperature T_2 into a small system at temperature T_1, under finite temperature difference. We consider the final state for the system, and assume this state was reached by a reversible isobaric process, then

$$\Delta S_1 = S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} \frac{\dj Q_r}{T} = \int_{T_1}^{T_2} \frac{C_P dT}{T} = C_P \ln \frac{T_2}{T_1}$$

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assuming C_P is relatively constant over the temperature range. Now we consider the final state for the reservoir. The heat flow in the actual irreversible process is $Q = C_P(T_2 - T_1)$. We instead consider a reversible isothermal process, but involving the same quantity of heat, then

$$\Delta S_2 = -\frac{Q}{T_2} = -\frac{C_P(T_2 - T_1)}{T_2}$$

Hence,

$$\Delta S = \Delta S_1 + \Delta S_2 = C_P \left(\ln \frac{T_2}{T_1} - \frac{T_2 - T_1}{T_2} \right) \geq 0$$

e.g. Free gas expansion. An equivalent reversible process is an isothermal reversible expansion involving a piston being pushed out slowly by the gas. This results in the system doing work while absorbing the same quantity of heat. From the first law,

$$đQ = dU + PdV = PdV$$

$$\Rightarrow dS = \frac{P}{T}dV = nR\frac{dV}{V}$$

as $TdS = đQ_r$. Hence,

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

Maxwell Relations

In this section we will use the central equation of thermodynamics to derive the Maxwell relations.

Central Equation of Thermodynamics: From the first law, $dU = đQ + đW$. Consider a reversible infinitesimal process, then

$$đQ_r = TdS \ , \ đW = -PdV$$

and hence

$$TdS = dU + PdV$$

which is the *Central Equation of Thermodynamics*, and which holds for any process.

Definition: (Helmholtz Free Energy) The *Helmholtz free energy F* is defined as

$$F = U - TS$$

Definition: (Gibbs Free Energy) The *Gibbs free energy G* is defined as

$$G = H - TS$$

Derivation of the Maxwell Relations:

- From the central equation, we have $dU = TdS - PdV$. This suggests that we have $U = U(S, V)$, giving

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

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

Now, for the differential form of U to be exact we must have

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

- We have that the enthalpy $H = U + PV$, so $dH = dU + PdV + VdP$

$$\Rightarrow dH = TdS + VdP$$

using the central equation. This implies that $H = H(S, P)$, so

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

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

and for the differential form of H to be exact,

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

- We have that the Helmholtz free energy $F = U - TS$, so $dF = dU - TdS - SdT$

$$\Rightarrow dF = -PdV - SdT$$

using the central equation. This implies that $F = F(V, T)$, so

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

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

and for the differential form of F to be exact,

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

- We have that the Gibbs function $G = H - TS$, so $dG = dH - TdS - SdT$

$$\Rightarrow dG = VdP - SdT$$

using the central equation and definition of the enthalpy. This implies that $G = G(P, T)$, so

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

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

and for the differential form of G to be exact,

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

Maxwell Relations: Thus we have:

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

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

the *Maxwell relations*. These can be remembered using the following:

$$
\begin{array}{ccc}
 & -S & \\
P & & V \\
 & T &
\end{array}
$$

To construct each Maxwell relation, start at some point and go clockwise around three letters to obtain the left hand side. If you have both P and S, include a minus sign. Then move on one letter and count back anti-clockwise three letters, inserting a minus sign if you have both P and S.

Definition: (Thermodynamic Potentials) The internal energy, enthalpy, Helmholtz free energy and Gibbs free energy are known as the *thermodynamic potentials*. From our derivaton of the Maxwell relations we see that they have natural or characteristic variables as follows:

Thermodynamic Potential	Natural Variables
U	S, V
H	S, P
F	T, V
G	T, P

A complete thermodynamic description of a substance requires two independent equations: the equation of the state (e.g. a PVT surface) and the energy equation (eg. UVT surface; see later). However if a thermodynamic potential is known as a function of its characteristic variables then we have a full thermodynamic description, e.g. for $F = F(T, V)$ the equation of state is derived from $\left(\frac{\partial F}{\partial V}\right)_T = -P$. The relationships of this form between the potentials and the state variables P, V etc. can be thought of as being similar to the relationship between the potentials and fields in electromagnetic theory.

Some Heat Capacity Results

We can now derive some useful expressions involving the heat capacities at constant volume and pressure.

Constant Volume Heat Capacity: From the central equation, we have $dU = TdS - PdV$, so for an isochoric process $dU = TdS = đQ_r$. Hence,

$$C_v = \frac{đQ_r}{dT} = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial T}\right)_V$$

$$\Rightarrow C_v = T\left(\frac{\partial S}{\partial T}\right)_V$$

Constant Pressure Heat Capacity: For a reversible isobaric process, $dH = TdS = đQ_r$, using our derivation of the second Maxwell relation. Hence,

$$C_p = \frac{đQ_r}{dT} = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial S}\right)_P \left(\frac{\partial S}{\partial T}\right)_P$$

$$\Rightarrow C_p = T\left(\frac{\partial S}{\partial T}\right)_P$$

Difference in Heat Capacities: For an ideal gas we had $C_p = C_v + nR$. We will now derive a similar relationship for a general PVT system. Let $S = S(T, V)$, then

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

We now divide by dT at constant pressure and multiply across by T:

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

$$\Rightarrow C_p = C_v + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\Rightarrow C_p = C_v + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

using a Maxwell relation, and we now use the cyclic relation

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P = -1$$

to obtain

$$C_p = C_v - T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2$$

We can relate this to the volume thermal expansivity $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ and the bulk modulus $\kappa = -V\left(\frac{\partial P}{\partial V}\right)_T$:

$$C_p = C_v + T\beta^2 \kappa V$$

Heat Capacity Derivatives: We have $C_v = T\left(\frac{\partial S}{\partial T}\right)_V$

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

using a Maxwell relation. Hence,

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

which can be thought of as the limiting value of heat absorption per unit temperature change as a function of the particular constant volume system.

Similarly, we can derive

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

Ratio of Heat Capacities: Now,

$$\frac{C_p}{C_v} = \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_V}$$

and we have the cyclic relations:

$$\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial T}{\partial P}\right)_S = -1 \Rightarrow \left(\frac{\partial S}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_S$$

$$\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial T}{\partial V}\right)_S = -1 \Rightarrow \left(\frac{\partial S}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_S$$

so

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

$$\Rightarrow \frac{C_p}{C_v} = \frac{\left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial T}{\partial P}\right)_S}$$

$$\Rightarrow \frac{C_p}{C_v} = \frac{\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial P}\right)_S} = \frac{\kappa_T}{\kappa_S}$$

using the isothermal and adiabatic compressibilities:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$

TdS **Equations:** The TdS equations are:

- $TdS = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$

- $TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$

- $TdS = C_v \left(\frac{\partial T}{\partial P}\right)_V dP + C_p \left(\frac{\partial T}{\partial V}\right)_P dV$

To derive the first, we start with $C_v = T\left(\frac{\partial S}{\partial T}\right)_V$ and write $S = S(T, V)$ in infinitesimal form:

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

$$\Rightarrow dS = \frac{C_v}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

using a Maxwell relation, and so

$$TdS = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

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To derive the second, we start with $C_p = T \left(\frac{\partial S}{\partial T} \right)_P$ and write $S = S(T, P)$ in infinitesimal form:

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

$$\Rightarrow dS = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

using a Maxwell relation, and so

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_P dP$$

To derive the third, we start with $S = S(P, V)$:

$$dS = \left(\frac{\partial S}{\partial P} \right)_V dP + \left(\frac{\partial S}{\partial V} \right)_P dV$$

$$\Rightarrow dS = \left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial T}{\partial P} \right)_V dP + \left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_P dV$$

$$\Rightarrow TdS = C_v \left(\frac{\partial T}{\partial P} \right)_V dP + C_p \left(\frac{\partial T}{\partial V} \right)_P dV$$

using our heat capacity definitions.

Other Thermodynamic Results

We here produce some thermodynamic results using the central equation, Maxwell's relations and the thermodynamic potentials U, H, F and G.

The Energy Equation: From the central equation,

$$dU = TdS - PdV$$

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

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

using a Maxwell relation. This is the energy equation. For an ideal gas, we find that $\left(\frac{\partial U}{\partial V} \right)_T = 0$, hence for an ideal gas $U = U(T)$ (whereas for other materials $U = U(T, V)$).

Entropy of an Ideal Gas: For an ideal gas, $U = U(T)$ and so $C_v = \left(\frac{\partial U}{\partial T} \right)_V = \frac{dU}{dT}$. Then we have

$$TdS = dU + PdV$$

$$\Rightarrow TdS = C_v dT + PdV$$

In molar terms, $Pv = RT$ and so

$$Tds = c_v dT + \frac{RT}{v} dv$$

$$\Rightarrow ds = c_v \frac{dT}{T} + R\frac{dv}{v}$$

$$\Rightarrow s = c_v \ln T + R \ln v + s_0$$

the ideal gas entropy per mole.

Enthalpy of a Chemical Reaction: Consider some chemical reaction, producing a volume change ΔV, absorbing heat Q and pushing piston with external pressure P_0. Then from the first law,

$$\Delta U = Q - P_0 \Delta V$$

$$\Rightarrow Q = \Delta U + P_0 \Delta V = \Delta U + \Delta(PV)$$

as $P = P_0 = $ constant. Hence,

$$Q = \Delta H$$

Work Done When No Net Temperature Change: Consider work performed by a system in thermal contact with its surroundings (at temperature T_0), but with the temperature of the system the same at the endpoints. For all such processes,

$$\Delta S + \Delta S_0 \geq 0$$

and for the surroundings

$$\Delta S_0 = -\frac{Q}{T_0}$$

$$\Rightarrow \Delta S - \frac{Q}{T_0} \geq 0$$

$$\Rightarrow Q - T_0 \Delta S \leq 0$$

$$\Rightarrow \Delta U + W - T_0 \Delta S \leq 0$$

from the first law, and so

$$\Delta(U - TS) + W \leq 0$$

$$\Rightarrow W \leq -\Delta F$$

hence the maximum work attainable for a system in thermal contact with a reservoir is minus the change in the Helmholtz potential.

Conditions For Equilibrium

We finish by briefly discussing some conditions for thermodynamic equilibrium.

Conditions for Equilibrium and Helmholtz Free Energy: Consider a constant volume system in thermal contact with a heat bath, which may undergo some irreversible process involving heat flow Q. To analyse this system, we instead consider a fully isothermal, isochoric process with the same endpoints. We have

$$\Delta S + \Delta S_0 \geq 0$$

and for the heat bath

$$\Delta S_0 = -\frac{Q}{T_0}$$

$$\Rightarrow \Delta S - \frac{Q}{T_0} \geq 0$$

$$\Rightarrow Q - T_0 \Delta S \leq 0$$

$$\Rightarrow \Delta U - T_0 \Delta S \leq 0$$

from the first law ($dV = 0$), and so

$$\Delta(U - TS) \leq 0$$

$$\Rightarrow \Delta F \leq 0$$

Hence the condition for thermodynamic equilibrium in a system in thermal contact with a heat reservoir and at constant volume is for F to be a minimum. This has the effect of maximising the entropy for the system and its surroundings.

Example: (Lattice Point Defects) Consider a crystal lattice of atoms. Given sufficient thermal energy an atom in the lattice will break free and either fill a vacancy elsewhere or become an interstitial (i.e. free) atom. Vacancies and interstitials are examples of point defects in the lattice. From the first law, one would expect the point defect population to be zero, as vacancies and interstitials cost extra energy, so having none minimises U. However, if the crystal is in thermal contact with a heat bath we instead must maximise the entropy of the entire system. For $F = U - TS$, the internal energy increases with each point defect, but so does the entropy. For increasing temperature, the TS term dominates, leading to large point defect populations and (eventually) melting.

Example: (Surface Tension) Consider a pipette attached to a reservoir of incompressible liquid at temperature T_0. A drop forms at the end of the pipette, with radius r and surface tension σ. From statics, the pressure inside the drop P is related to the external pressure P_0 by

$$P = P_0 + \frac{2\sigma}{r}$$

Hence at equilibrium, the reservoir must be put under pressure P when the drop is experiencing pressure P_0. Now consider an isothermal, reversible expansion of the drop from r to $r + dr$. The volume change is then

$$dV = 4\pi r^2 dr$$

and hence

$$dW = (P - P_0)dV = \frac{2\sigma}{r} 4\pi r^2 dr$$

$$\Rightarrow dW = 8\pi \sigma r dr$$

and this is clearly the change dF in the free energy of the entire system, from $W = -\Delta F$. Now, for the reservoir, with per unit volume free energy f_0, we have

$$dF_{\text{res}} = -f_0 dV = -4\pi f_0 r^2 dr$$

and as

$$dF_{\text{total}} = dF_{\text{res}} + dF_{\text{drop}}$$

we have

$$dF_{\text{drop}} = \left(\frac{\partial F_{\text{drop}}}{\partial r}\right)_T = 4\pi f_0 r^2 dr + 8\pi \sigma r dr$$

and upon integrating
$$F_{\text{drop}} = \frac{4}{3}\pi r^3 f_0 + 4\pi r^2 \sigma$$
showing that F is minimised by a spherical drop.

Conditions for Equilibrium and Gibbs Free Energy: Consider a constant pressure system in thermal contact with a heat bath, which may undergo some irreversible process involving heat flow Q. To analyse this system, we instead consider a fully isobaric, isochoric process with the same endpoints. We have
$$\Delta S + \Delta S_0 \geq 0$$
and for the heat bath
$$\Delta S_0 = -\frac{Q}{T_0}$$
$$\Rightarrow \Delta S - \frac{Q}{T_0} \geq 0$$
$$\Rightarrow Q - T_0 \Delta S \leq 0$$
$$\Rightarrow \Delta U + P_0 \Delta V - T_0 \Delta S \leq 0$$
from the first law, and as $\Delta P = \Delta T = 0$ we have
$$\Delta U + \Delta(PV) - \Delta(TS) \leq 0$$
$$\Delta(U + PV - TS) \leq 0$$
$$\Rightarrow \Delta G \leq 0$$
Hence the condition for thermodynamic equilibrium in a system in thermal contact with a heat reservoir and at constant pressure is for G to be a minimum.

Now, as we must have $\Delta G \leq 0$ or
$$\Delta H - T_0 \Delta S \leq 0$$
for the process to proceed we can consider the different possibilites for the signs of ΔH and ΔS: if $\Delta H > 0$ and $\Delta S < 0$ the process cannot occur; if $\Delta H < 0$ and $\Delta S > 0$ the process may occur; if both have the same sign then they balance, with the dominant term dependent on the magnitude of T_0.

As $G = T - TS$ and $F = U - TS$ then $G = F + PV$ and so
$$\Delta G = \Delta F + \Delta(PV)$$
it follows that G and F are interchangable for systems where $\Delta(PV) \approx 0$, i.e. often for solid systems, but not for gas systems.

Summary of Equilibrium Conditions:

System	Condition
Totally isolated	S a maximum
Thermally isolated, constant P	H a minimum
Thermally isolated, constant V	U a minimum
Connected to heat bath, constant V	F a minimum
Connected to heat bath, constant P	G a minimum

Note that all these conditions in the end amount to maximising the entropy for the system and surroundings.