Thermal Physics

Temperature

Temperature is the property of objects that is the same when they are in thermal equilibrium.

Zeroth Law of Thermodynamics: If object A is in thermal equilibrium with B and if A is in thermal equilibrium with object C, then the temperatures of B and C are equal and they are in thermal equilibrium with each other

Kinetic Theory of Gases

- Any macroscopic volume of gas contains a very large number of molecules
- Molecules are separated by distances large compared with their own dimensions and are in continuous motion
- Assume molecules exert no forces on one another except when they collide
- All collisions are perfectly elastic
- In the absence of external forces the molecules are distributed uniformly
- Directions of molecular velocities are assumed to be distributed uniformly

Molecular Flux

Molecular Flux is the total number of molecules arriving at a surface per unit area per unit time.

$$\Delta\Phi = \frac{\Delta N}{\Delta A \Delta t}$$

From increment of surface of sphere:

$$\Delta A = r^2 \sin\theta \, \Delta\theta\Delta\phi$$

Number of particles crossing per unit of surface area of sphere:

$$\frac{N}{4\pi r^2}$$

Number of particles with polar angle between θ and $\theta + \Delta\theta$ and azimuthal angle between ϕ and $\phi + \Delta\phi$:

$$\begin{aligned} \Delta N_{\theta\phi} &= \frac{N_{\Delta A}}{4\pi r^2}\Delta A \\ \Delta N_{\theta\phi} &= \frac{N_{\Delta A}}{4\pi r^2} r^2 \sin\theta \, \Delta\theta\Delta\phi \\ \Delta N_{\theta\phi} &= \frac{N_{\Delta A}}{4\pi} \sin\theta \, \Delta\theta\Delta\phi \end{aligned}$$

Add restriction that particles must also have velocity between v and $v + \Delta v$, hence they must fit inside the volume of a cylinder of length $v\Delta t$ and area $\Delta A \cos\theta$:

$$\Delta N_{\theta\phi v} = \frac{\Delta n_v}{4\pi}(\sin\theta\, \Delta\theta\Delta\phi)(\Delta A \cos\theta\; v\Delta t)$$

Taking the flux for this number of molecules:

$$\begin{aligned}
\Delta\Phi_{\theta\phi v} &= \frac{\Delta N}{\Delta A \Delta t} \\
\Delta\Phi_{\theta\phi v} &= \frac{\frac{1}{4\pi} v\Delta n \sin\theta \cos\theta\; \Delta\theta\Delta\phi\Delta A\Delta t}{\Delta A \Delta t} \\
\Delta\Phi_{\theta\phi v} &= \frac{1}{4\pi} v\Delta n \sin\theta \cos\theta\; \Delta\theta\Delta\phi
\end{aligned}$$

Integrating over θ and ϕ:

$$\begin{aligned}
\Delta\Phi_v &= \int_0^{2\pi}\int_0^{\frac{\pi}{2}} \frac{1}{4\pi} v\Delta n \sin\theta\cos\theta\; d\theta d\phi \\
&= \frac{1}{4\pi} v\Delta n \left[\int_0^{\frac{\pi}{2}} \phi \sin\theta\cos\theta\; d\theta\right]_0^{2\pi} \\
&= \frac{1}{4\pi} v\Delta n \int_0^{\frac{\pi}{2}} 2\pi \sin\theta\cos\theta\; d\theta \\
&= \frac{1}{2} v\Delta n \int_0^{\frac{\pi}{2}} \sin\theta\cos\theta\; d\theta \\
&= \frac{1}{2} v\Delta n \int_0^{\frac{\pi}{2}} \frac{1}{2}\sin 2\theta\; d\theta \\
&= \frac{1}{2} v\Delta n \left[-\frac{1}{4}\cos 2\theta\right]_0^{\frac{\pi}{2}} \\
&= \frac{1}{2} v\Delta n \left[\left(-\frac{1}{4}(-1)\right) - \left(-\frac{1}{4}(1)\right)\right] \\
&= \frac{1}{2} v\Delta n \left[\left(\frac{1}{4}\right) + \left(\frac{1}{4}\right)\right] \\
\Delta\Phi_v &= \frac{1}{4} v\Delta n
\end{aligned}$$

Total molecular flux is given by substituting in average speed and total number of molecules n:

$$\Phi = \frac{1}{4}\bar{v}n$$

Principle of Equipartion

At temperature T, the average energy of any degree of freedom is always equal to $\frac{1}{2}kT$. This applies to all f degrees of freedom, including translational motion, rotational, vibrational, elastic, etc.

From this it follows that the total energy of a system is given by the number of molecules N times the number of degrees of freedom for each molecules, time the average energy per degree of freedom:

$$U_{thermal} = N \times f \times \frac{1}{2} kT$$

$$U_{thermal} = \frac{f}{2} NkT$$

Note that an Einstein solid has six degrees of freedom (three kinetic, three potential).

First Law of Thermodynamics

Change in internal energy is equal to the amount of energy that enters the system as heat plus the amount of work done on the system.

$$\Delta U = Q + W$$

Work done *on* a system is defined as W > 0
Work done *by* the system has W < 0
Q > 0 if heat flows *into* the system
Q < 0 if heat flows *out of* the system

The work done *on* the system is defined as:

$$W = -\int_{V_a}^{V_b} P(V)\, dV$$

Types of Processes

Isochoric processes

These are easy, as V is constant therefore W is always zero:

$$W = 0$$

Isobaric processes

These are also easy, as P is constant therefore the integral is simply:

$$W = -P(V_b - V_a)$$

Isothermal processes

These are more complicated, as we need to write P as a function of V. From the ideal gas law we know that $P = \frac{NkT}{V}$. Hence we can write (note that by definition T is constant):

$$\begin{aligned} W &= -\int_{V_a}^{V_b} \frac{NkT}{V} dV \\ &= -NkT \int_{V_a}^{V_b} \frac{1}{V} dV \\ &= -NkT(\log V_b - \log V_a) \\ W &= -NkT \log\left(\frac{V_b}{V_a}\right) \end{aligned}$$

Adiabatic Processes

An adiabatic process occurs when there is no flow of heat. Here temperature will not be constant. Since there is no heat flow we can write:

$$\Delta U = Q + W = -P\Delta V$$

From the equipartition theorem we know that:

$$\Delta U = \frac{f}{2} Nk\Delta T$$

Combining these equations we have:

$$-P\Delta V = \frac{f}{2} Nk\Delta T$$

Using the ideal gas law to substitute for P:

$$\begin{aligned} -\frac{NkT}{V}\Delta V &= \frac{f}{2} Nk\Delta T \\ -\frac{T}{V}\Delta V &= \frac{f}{2}\Delta T \\ -\frac{\Delta V}{V} &= \frac{f}{2}\frac{\Delta T}{T} \end{aligned}$$

Integrate both sides to find total changes in V and T:

$$\begin{aligned} -\int_{V_a}^{V_b} \frac{1}{V} dV &= \frac{f}{2} \int_{T_a}^{T_b} \frac{1}{T} dT \\ -(\log V_b - \log V_a) &= \frac{f}{2}(\log T_b - \log T_a) \\ -\log\left(\frac{V_b}{V_a}\right) &= \frac{f}{2} \log\left(\frac{T_b}{T_a}\right) \\ \log\left(\frac{V_a}{V_b}\right) &= \log\left(\frac{T_b{}^{\frac{f}{2}}}{T_a{}^{\frac{f}{2}}}\right) \\ \frac{V_a}{V_b} &= \frac{T_b{}^{\frac{f}{2}}}{T_a{}^{\frac{f}{2}}} \end{aligned}$$

$$V_a T_a^{\frac{f}{2}} = V_b\, T_b^{\frac{f}{2}}$$

Another way of expressing this is simply to write:

$$VT^{\frac{f}{2}} = constant$$

If N is constant, we can use the ideal gas law to substitute in for T and write:

$$\begin{aligned} V\left(\frac{PV}{Nk}\right)^{\frac{f}{2}} &= constant \\ V^{\frac{f+2}{2}} P^{\frac{f}{2}} &= constant \\ V^{\frac{f+2}{f}} P &= constant \\ V^{\gamma} P &= constant \end{aligned}$$

Where $\gamma = \frac{f+2}{f}$ is known as the adiabatic constant

Heat Capacity

The heat capacity is the amount of heat needed to raise the temperature of a given amount of a given substance by one degree.

$$C = \frac{Q}{\Delta T}$$

The specific heat capacity is the heat capacity per unit mass:

$$c = \frac{Q}{\Delta T m}$$

Specific heat capacity is a context-specific measure, as it depends on whether you are also doing work on the substance. Obviously, the more work is being done, the less heat needs to be added in order to raise the body's temperature.

Enthalpy

The enthalpy of a system is the total amount of energy one would need in order to spontaneously create that system and make room for it in an atmosphere of 1atm. It can be written as:

$$\begin{aligned} H &= U + W \\ H &= U + PV \end{aligned}$$

Generally P is taken to be constant and V is the volume occupied by the system. If P is constant, it becomes much more convienient to talk about enthalpy than energy. This can be seen as follows.

If we want to talk about the change in internal energy of a process, the expression is:

$$\Delta U = Q + W_{total}$$

$$\Delta U = Q - P\Delta V + W_{other}$$

Where W_{total} has been divided into the compression-expansion work of the atmosphere, and any other work being done on the system. In contrast, if we talk about change in enthalpy, the expression is:

$$\begin{aligned}
\Delta H &= \Delta U + P\Delta V \\
\Delta H &= Q - P\Delta V + W_{other} + P\Delta V \\
\Delta H &= Q + W_{other}
\end{aligned}$$

In essence, therefore, change in enthalpy is just change in internal energy minus the effects of changing volume of the system. Indeed, if W_{other} is constant, as it often is, we can simply say that ΔH is equal to Q, the heat flow. We can ignore the effects of changing or shrinking system volume.

It turns out that the heat capacity at constant pressure C_P can be given as:

$$C_P = \frac{\partial H}{\partial T}$$

Thermal Conductivity of Gases

Mean free path is the average distance travelled by a molecule before making its first collision

$$l = \frac{1}{n\sigma} = \frac{1}{n\pi d^2}$$

Where σ is the cross-sectional area of one target molecule, and d is the diameter of said molecule

The survival equation is an expression giving the number of surviving molecules at distance x:

$$N(x) = N_0 e^{-\frac{x}{l}}$$

The thermal conductivity of a gas is defined as:

$$k_t = \frac{1}{3} n\bar{v}c_v l = \frac{1}{3}\frac{c_v\bar{v}}{\sigma}$$

k_t is always proportional to $\sqrt{T}$

Very Large Numbers

Very large numbers have some interesting properties.

$$\begin{aligned}
\log\left(10^{10^{23}} \times 10^{23}\right) &= \log\left(10^{10^{23}}\right) + \log(10^{23}) \\
&= 10^{23}\log(10) + 23\log(10) \\
&= \log(10)\,(10^{23} + 23) \\
&\approx 10^{23}\log(10) \\
\log\left(10^{10^{23}} \times 10^{23}\right) &\approx \log\left(10^{10^{23}}\right)
\end{aligned}$$

$$10^{10^{23}} \times 10^{23} \approx 10^{10^{23}}$$

Thus, when we multiply a very large number by an astronomically large number, the value is effectively unchanged.

Macrostates and Microstates

Consider tossing identical coins. One cannot distinguish one coin from another other; you can only distinguish the final outcome, that is the number of heads and tails. The macrostate refers to this observable quality - the number of heads and tails. Microstates are the unobservable different ways that a macrostate can be constructed. For example, HHTT and HTHT have the same macrostate (2 heads 2 tails), but different microstates. The multiplicity Ω is the total number of microstates for a given macrostate.

Einstein Solid

The multiplicity of a macrostate with q energy units and N oscillators is given as:

$$\Omega(N,q) = \frac{(q+N-1)!}{q!\,(N-1)!}$$

Ideal Gas

The multiplicity of a macrostate of an ideal gas with volume V and N particles of mass m, and h representing planck's constant, is given by:

$$\Omega(U,V,N) = \frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!}\sqrt{2mU}^{3N}$$

$$\Omega(U,V,N) = f(N)V^N U^{3N/2}$$

Probability of Spontaneous Vacuum

Consider the probability of a vacuum of size ΔV spontaneously developing in a room of size V.

$$\begin{aligned} P &= \frac{\Omega(U,V-\Delta V,N)}{\Omega(U,V,N)} \\ &= \frac{f(N)(V-\Delta V)^N U^{3N/2}}{f(N)V^N U^{3N/2}} \\ &= \frac{(V-\Delta V)^N}{V^N} \end{aligned}$$

If $N = 10^{28}, V = 500, \Delta V = 10^{-6}$

$$P = \left(\frac{500 - 10^{-6}}{500}\right)^{10^{28}}$$

$$P = (0.999999998\,)^{10^{28}}$$

$$P = (9.99999998\,)^{-10^{28}}$$

Alternatively using the approximation $\log(1+x) \approx x$ for small x, we derive:

$$\begin{aligned}\log(P) &= N\log\left(\frac{V-\Delta V}{V}\right)\\ &= N\log\left(1-\frac{\Delta V}{V}\right)\\ &\approx N\left(\frac{\Delta V}{V}\right)\\ &= 10^{28}\left(\frac{10^{-6}}{500}\right)\\ &= 10^{28}\times 2\times 10^{-9}\\ &= 2\times 10^{-19}\\ P &= 10^{2\times 10^{-19}}\end{aligned}$$

Interacting Systems

The multiplicity of a macrostate involving two interacting systems is simply the product of their individual multiplicities:

$$\Omega_{total} = \Omega_A\Omega_B$$

Consider two weakly coupled (exchanging only energy) Einstein solids. Using the high T approximation:

$$\begin{aligned}\Omega &= \left(\frac{eq_A}{N}\right)^N\left(\frac{eq_B}{N}\right)^N\\ &= \left(\frac{e}{N}\right)^{2N}(q_a q_B)^N\end{aligned}$$

Since $q = q_A + q_B$ we can write:

$$\Omega = \left(\frac{e}{N}\right)^{2N}\big(q_a(q-q_A)\big)^N$$

$$\Omega = \left(\frac{e}{N}\right)^{2N}(q_a q - q_a^2)^N$$

The peak of this multiplicity function will occur, as always, when $\frac{\partial\Omega}{\partial q_a} = 0$. Hence:

$$\begin{aligned}\frac{\partial\Omega}{\partial q_a} &= N\left(\frac{e}{N}\right)^{2N}(q_a q - q_a^2)^{N-1}(q-2q_a)\\ 0 &= (q_a q - q_a^2)^{N-1}(q-2q_a)\\ q_a q &= q_a^2 \text{ or } q = 2q_a\\ q_a &= \frac{q}{2}\end{aligned}$$

This tells us that multiplicity is maximised when energy is shared exactly evenly between the two solids!

$$\Omega_{\max} = \left(\frac{e}{N}\right)^{2N}\left(\frac{q}{2}\right)^{2N}$$

Let's now consider the multiplicity if we shift just a small amount Δq of the energy from one solid to the other:

$$\Omega = \left(\frac{e}{N}\right)^{2N}\left(\left(\frac{q}{2}+\Delta q\right)\left(\frac{q}{2}-\Delta q\right)\right)^{N}$$

$$\Omega = \left(\frac{e}{N}\right)^{2N}\left(\left(\frac{q}{2}\right)^{2}-\Delta q^{2}\right)^{N}$$

$$\log(\Omega) = 2N\log\left(\frac{e}{N}\right) + N\log\left(\left(\frac{q}{2}\right)^{2}-\Delta q^{2}\right)$$

$$\log(\Omega) = 2N\log\left(\frac{e}{N}\right) + N\log\left(\left(\frac{q}{2}\right)^{2}\left(1-\frac{4\Delta q^{2}}{q^{2}}\right)\right)$$

$$\log(\Omega) = 2N\log\left(\frac{e}{N}\right) + 2N\log\left(\frac{q}{2}\right) + N\log\left(1-\frac{4\Delta q^{2}}{q^{2}}\right)$$

$$\log(\Omega) \approx 2N\log\left(\frac{e}{N}\right) + 2N\log\left(\frac{q}{2}\right) - N\frac{4\Delta q^{2}}{q^{2}}$$

$$\Omega = \left(\frac{e}{N}\right)^{2N}\left(\frac{q}{2}\right)^{2N} e^{-N\left(\frac{2(\Delta q)}{q}\right)^{2}}$$

$$\Omega = \Omega_{\text{max}} e^{-N\left(\frac{2(\Delta q)}{q}\right)^{2}}$$

Our new Ω will fall to $\frac{1}{e}\Omega_{\text{max}}$ when:

$$N\left(\frac{2(\Delta q)}{q}\right)^{2} = 1$$

$$\frac{2(\Delta q)}{q} = \sqrt{\frac{1}{N}}$$

$$\Delta q = \frac{q}{2\sqrt{N}}$$

Even if $q \approx N$, this number will be tiny. It will be even smaller in this case because for a high temperature system $q \gg N$. From this we can conclude that Δq will be very small, and hence any fluctuations away from Ω_{max} will be far too small to measure.

Second Law of Thermodynamics

Any large system in equilibrium will be found in the macrostate with the greatest multiplicity (aside from fluctuations that are normally too small to measure). Hence, multiplicity tends to increase.

Entropy is just a more convenient way of talking about multiplicity. It is defined as:

$$S = k_B \log(\Omega)$$

Processes where entropy increases are said to be irreversible. Isentropic processes are those which leave the entropy of the universe unchanged - they are reversible. Heat transfer is always irreversible, while quasistatic, adiabatic compression or expansion is reversible (as no heat transferred).

Entropy and Temperature

We know that in equilibrium, the entropy of a system will be maximised. This means that the following condition must hold:

$$\frac{\partial S_a}{\partial U_a} = \frac{\partial S_b}{\partial U_b}$$

If this were not the case, then total entropy could increase by heat flowing from body a to body b (or vice-verse), and hence entropy would not be maximised. The significance of this is that we have just found something that is the same for two bodies in thermal equilibrium: the derivative of entropy with respect to internal energy.

What else can we say about this quantity? SInce S has units of J/K, the derivative of S with respect to U will have units of K^{-1}. We also know that entropy is increased if it flows from a body with a shallow slope to one with a steep slope; hence we know that energy will tend to flow to bodies with a high derivative of S with respect to U. Putting all these pieces together, the following definition becomes obvious:

$$T = \left(\frac{\partial S}{\partial U}\right)^{-1}$$

With this definition, temperature has all the usual properties: units of K, energy tends to flow to bodies with low T (and hence high slope), and two bodies in thermal equilibrium have the same T.

Verification with Einstein Solid

$$\begin{aligned} S &= k\log(\Omega) \\ &= k\log\left(\left(\frac{eq}{N}\right)^N\right) \\ &= kN\log\left(\frac{eq}{N}\right) \\ &= kN\left[\log e + \log\left(\frac{q}{N}\right)\right] \\ &= Nk\left[\log\left(\frac{q}{N}\right) + 1\right] \\ S &= Nk\left[\log\left(\frac{q}{N}\right) + 1\right] \end{aligned}$$

U is just equal to ϵq, where ϵ is some constant (energy per energy unit):

$$\begin{aligned} &S = Nk\left[\log\left(\frac{U}{\epsilon N}\right) + 1\right] \\ &S = Nk\log(U) - Nk\log(\epsilon N) + Nk \\ &\frac{\partial S}{\partial U} = \frac{Nk}{U} \end{aligned}$$

Hence temperature is given by:

$$T = \frac{1}{\frac{\partial S}{\partial U}} = \frac{U}{Nk}$$

This is exactly what is predicted from the equipartition theroem:

$$U = NkT$$

Measuring Entropy

Given the definition of temperature:

$$T = \frac{1}{\frac{\Delta S}{\Delta U}}$$

We can rearrange to find:

$$\Delta S = \frac{\Delta U}{T}$$

Since it is usually fairly easy to measure ΔU and T, we can thus measure the change in entropy. This can be written in terms of heat capacity C_V:

$$\Delta S = \frac{C_V dT}{T}$$

We can integrate to get the full change in entropy:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T} dT$$

Thermodynamic Identity

Consider a system in which the internal energey U and volume V are both changing. The total entropy change of the system is thus given as the sum of the entropy changes caused by each of these processes:

$$\Delta S = \Delta S_U + \Delta S_V$$
$$\Delta S = \frac{\Delta S_U}{\Delta U}\Delta U + \frac{\Delta S_V}{\Delta V}\Delta V$$

Converting to infinitesimals:

$$dS = \frac{\partial S}{\partial U} dU + \frac{\partial S}{\partial V} dV$$

Substituting in the known relationships between entropy and energy and entropy and volume:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

This formula holds so long as other variables like N are held constant.

Efficiency

Efficiency is simply defined as the ratio of the useful work produced and the heat energy absorbed:

$$\begin{aligned}\epsilon &= \frac{benefit}{cost}\\ &= \frac{W}{Q_H}\\ &= \frac{Q_H - Q_C}{Q_H}\\ \epsilon &= 1 - \frac{Q_C}{Q_H}\end{aligned}$$

Heat Engines

A heat engine is any device that absorbs heat and converts part of this absorbed energy into work. Over the course of a cycle, the entropy of a heat engine does not change, as the entropy of an ideal gas depends only on N, T and V, all of which are the same after any full cycle. However, the heat engine does reduce the entropy of the source of its heat, and increase the entropy at the sink of its heat. For heat flow to occur, $T_{source} > T_{sink}$.

$$\begin{aligned}\Delta S_H &= -\frac{Q_H}{T_H}\\ \Delta S_C &= -\frac{Q_C}{T_C}\end{aligned}$$

In order to satisfy the second law of thermodynamics:

$$\begin{gathered}\Delta S_H \leq \Delta S_C\\ \frac{Q_H}{T_H} \leq \frac{Q_C}{T_C}\\ \frac{T_C}{T_H} \leq \frac{Q_C}{Q_H}\end{gathered}$$

The efficiency of a heat engine is defined as:

$$\begin{aligned}\epsilon &= 1 - \frac{Q_C}{Q_H}\\ \frac{Q_C}{Q_H} &= 1 - \epsilon\end{aligned}$$

Combining these expressions:

$$\frac{T_C}{T_H} \leq 1 - \epsilon$$
$$\epsilon \leq 1 - \frac{T_C}{T_H}$$

Carnot Cycle

The Carnot cycle is a theoretical thermodynamic cycle that is the most efficient cycle for converting a given amount of thermal energy into work, or conversely, creating a temperature difference (e.g. refrigeration) by doing a given amount of work.

To minimize ΔS we need to absorb Q at constant T. So use an isothermal expansion for this. We need to cool the engine to TC to minimize the entropy gain , do an Adiabatic expansion until T = TC. Then do an isothermal compression at T = TC to let the heat flow out. Do an adiabatic compression back to T = TH and we're back to the start.

As always, the efficiency of a carnot engine is given by:

$$\epsilon = \frac{W}{Q_H}$$

The first two stages of a carnot cycle will do positive work, while the second two will do negative work (i.e. the environment does work on the system), so we can write the efficiency relation as:

$$\epsilon = \frac{W_1 + W_2 - W_3 - W_4}{Q_1}$$

Note that $Q_H = Q_1$ because this is the stage when heat is being absorbed from the hot region. We also know something else about Q_1; we know that the temperature of the system is constant, and hence $\Delta U = 0$. This is only possible if the system expends all incoming heat energy in the form of work:

$$W_1 = Q_1$$

In other words, all heat that is absorbed by the system is used by the system to do work on its environment. Hence we can write:

$$\epsilon = \frac{W_1 + W_2 - W_3 - W_4}{W_1}$$
$$\epsilon = 1 + \frac{W_2 - W_3 - W_4}{W_1}$$

Consider know the two adiabatic processes in stages 2 and 4. We know that for an adiabatic process $Q = 0$, and so it follows that:

$$\Delta U = W$$
$$\frac{f}{2} Nk\Delta T = W$$

Hence, the work done in stages 2 and 4 depends only on the temperature change. But the temperature change is exactly the same in both cases, with only the direction differing. This means that $W_2 - W_4 = 0$, and hence we can simplify our overall expression as:

$$\epsilon = 1 - \frac{W_3}{W_1}$$

Now all we need to do is calculate W_3 and W_1. Since these are both isothermal processes, we can use the equation derived earlier:

$$W_1 = -NkT_1 \log\left(\frac{V_b}{V_a}\right)$$
$$W_3 = -NkT_2 \log\left(\frac{V_c}{V_d}\right)$$

Substituting in these expressions and simplifying:

$$\epsilon = 1 - \frac{NkT_2 \log\left(\frac{V_c}{V_d}\right)}{NkT_1 \log\left(\frac{V_b}{V_a}\right)}$$
$$\epsilon = 1 - \frac{T_2 \log\left(\frac{V_c}{V_d}\right)}{T_1 \log\left(\frac{V_b}{V_a}\right)}$$

From the adiabatic formulas we know that:

$$\frac{V_c}{V_b} = \frac{T_H{}^{\frac{f}{2}}}{T_L{}^{\frac{f}{2}}}$$
$$\frac{V_a}{V_d} = \frac{T_H{}^{\frac{f}{2}}}{T_L{}^{\frac{f}{2}}}$$

Hence:

$$\frac{V_c}{V_b} = \frac{V_d}{V_a}$$
$$\frac{V_c}{V_d} = \frac{V_b}{V_a}$$
$$\log\left(\frac{V_c}{V_d}\right) = \log\left(\frac{V_b}{V_a}\right)$$

Thus the expression simplifies to the familiar:

$$\epsilon = 1 - \frac{T_2}{T_1}$$

Refrigerator

A refrigerator is conceptually simply the opposite of a heat engine: instead of using the flow of heat to generate work, it uses an input of work to generate a reverse flow of heat. The 'efficiency' of a refrigerator is called the coefficient of performance, and is defined as:

$$COP = \frac{benefit}{cost}$$
$$= \frac{Q_C}{W}$$
$$COP = \frac{Q_C}{Q_H - Q_C}$$

Helmholtz Free Energy

In many cases in the real world, we aren't interested in the volume needed to be created - for example in constant volume processes. However, often the temperature differs between object and surroundings, which means that there will be some heat flow (and hence entropy increase) as a result of creating the system. The Helmholtz free energy combines these two insights, and is defined as:

$$F = U - TS$$

Remember that for a quasistatic process, $Q = T\Delta S$, so this simplifies to:

$$F = U - Q$$

In other words, the Helmholtz free energy is the total internal energy of a system, minus the amount of energy that would come from the flow of heat from its environment. Effectively, subtracting off TS is an adjustment for the fact that if we were to create the system from scratch, we would not need to start with the entirety of U, as some energy would come for free by the flow of heat.

Helmholtz free energy is relevant for processes that occur at constant temperature and constant volume.

Gibbs Free Energy

Gibbs free energy is an extension of Helmholtz free energy that also incorporates the work needed to be done to create the volume needed to contain a system. It is equal to the enthalpy minus the heat flow:

$$G = U - TS + PV$$

Gibbs free energy is relevant for processes that occur at constant temperature and constant pressure.

Phase Transformations

A phase change is a discontinuous change in the properties of a substance when its environment is only changed infinitesimally. These transitions can be plotted on a phase diagram, showing the phase a substance is in for every combinatioun of pressure and temperature. Some important points on a phase diagram include the triple point, where solid, liquid, and gas can all exist simultaneously in equilibrium, and the critical point, where there is no longer a distinct difference between liquid and gas.

Taking the formula for Gibbs free energy and differentiating with respect to T, holding P and N constant:

$$\frac{\partial G}{\partial T} = -S$$

Gases have more entropy than liquids, which in turn have more entropy than solids. Thus, the $\frac{\partial G}{\partial T}$ slopes for the three different phases will differ, which means the lines will intersect at various points. This in turn means that depending on the temperature, a different phase will have the lowest G, and hence will exist in equilibrium.

We can apply the same analysis to how G changes with P, holding T constant:

$$\frac{\partial G}{\partial P} = V$$

Since the volume of gas is greater than that of liquid, which is greater than that of a solid (usually), we will again have three different slopes, and hence three different preferred phases depending on the pressure.

Clausius-Clapeyron Relation

Along a phase boundary for a given substance, we know that the Gibbs free energy must be the same for either phase - otherwise both could not coexist at equilibrium. Consider the phase boundary between liquid and gas. We can write this relation as:

$$\begin{aligned} G_l &= G_g \\ U_l - TS_l + PV_l &= U_g - TS_g + PV_g \end{aligned}$$

Take the differential change in this relation as P and T change by very small amounts:

$$\begin{aligned} -S_l dT + V_l dP &= -S_g dT + V_g dP \\ V_l dP - V_g dP &= -S_g dT + S_l dT \\ dP\left(V_l - V_g\right) &= dT\left(S_l - S_g\right) \\ \frac{dP}{dT} &= \frac{S_l - S_g}{V_l - V_g} \\ \frac{dP}{dT} &= \frac{\Delta S}{\Delta V} \end{aligned}$$

This can also be written as (where L is the latent heat):

$$\frac{dP}{dT} = \frac{Q/T}{\Delta V}$$

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

Solving for P:

$$\Delta V dP = \frac{L}{T} dT$$
$$\int \frac{NkT}{P} dP = \int \frac{L}{T} dT$$
$$\int \frac{Nk}{P} dP = \int \frac{L}{T^2} dT$$
$$Nk \log(P) = -\frac{L}{T} + c$$
$$\log(P) = -\frac{L}{TNk} + \frac{c}{Nk}$$
$$P = e^{-\frac{L}{TNk} + \frac{c}{Nk}}$$
$$P = Ae^{-\frac{L}{TNk}}$$