The Second Law of Thermodynamics

Statements of the 2nd Law of Thermodynamics

**Kelvin’s statement** – No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion to work.

*Picture of heat engine attempting to violate Kelvin’s statement*

\[
q_H + w \neq 0
\]

**Clausius’ statement** – It is not possible for heat to flow from a colder body to a warmer body without any work having been done.

*Picture of heat engine attempting to violate Clausius’ statement*

\[
q_H + q_C \neq 0
\]

**Standard chemist’s statement** – The entropy of an isolated system increases in the course of a spontaneous change. \( \Delta S_{\text{Total}} > 0 \) where \( S_{\text{Total}} \) is the total entropy of the isolated system of interest.

Defining the isolated system is vital to using the second law of thermodynamics as a predictor of change. We assume universe is isolated so the second law becomes

\[
\Delta S_{\text{Universe}} > 0
\]
Some energy must be wasted in the form of work (if we desire cooling from our energy input) or heat (if we desire work from our energy input).

Ideal heat engines have $\Delta S_{\text{Total}} = 0$

*Other statements (for fun)*

Lucretius – Greek philosopher (1st century B.C.)
"For we see that anything can be more speedily disintegrated than put together again. Hence, what the long day of time, the bygone eternity, has already shaken and loosened to fragments could never in the residue of time be reconstructed."

Mother Goose
"Humpty Dumpty sat on a wall
Humpty Dumpty had a great fall
All the King's horses, and all the King's men
Couldn't put Humpty together again"

Gilbert N. Lewis (Notable Nebraskan☺)
1. "Every system which is left to itself will, on the average, change toward a condition of maximum probability"

2. "Every system left to itself changes, rapidly or slowly, in such a way as to approach a definite final state of rest. No system, except through the influence of external agencies, will change away from the state of equilibrium"

3. "Gain in information is loss in entropy"

T. S. Eliot – (poet: The Hollow Men – 1925)
"... this is the way the world ends
not with a bang, but with a whimper"

J. A. V. Butler (British electrochemist)
"There is a tendency in nature for energy to pass from more available to less available forms."
Max Planck (Father of quantum mechanics)
1. "It is impossible to diminish the entropy of a system of bodies without thereby leaving behind changes in other bodies."

2. "A transformation whose only final result is to transform into work heat extracted from a source which is at the same temperature throughout is impossible."

Enrico Fermi (Father of the nuclear reactor)
"The state of maximum entropy is the most stable state of an isolated system."

Arthur Eddington (Father of astrophysics)
"Entropy is time’s arrow"
\[
\frac{dS_{\text{Total}}}{dt} > 0
\]

Adiabatic Processes

Relationship between Volume and Temperature

\[
dU = dq + dw \Rightarrow dU = dw \Rightarrow C_v dT = -p_v dV \Rightarrow \int C_v dT = -\int p_v dV = -\int p dV
\]

\[
\Rightarrow \int C_v dT = -\int \frac{nRT}{V} dV \Rightarrow \int \frac{C_v}{T} dT = -\int \frac{nR}{V} dV \Rightarrow C_v \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1}
\]

\[
\Rightarrow C_v \ln \frac{T_2}{T_1} = nR \ln \frac{V_1}{V_2} = (C_p - C_v) \ln \frac{V_1}{V_2} \Rightarrow \ln \frac{T_2}{T_1} = \left(\frac{C_p - C_v}{C_v}\right) \ln \frac{V_1}{V_2}
\]

\[
\Rightarrow \ln \frac{T_2}{T_1} = \ln \left(\frac{V_1}{V_2}\right)^{\frac{(C_p - C_v)}{C_v}} \quad \text{Let} \quad \frac{C_p}{C_v} = \gamma \Rightarrow \ln \frac{T_2}{T_1} = \ln \left(\frac{V_1}{V_2}\right)^{\gamma - 1}
\]

\[
\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}
\]

\[
\gamma = \frac{C_p}{C_v} \quad \text{is the heat capacity ratio.}
\]
Relationship between Volume and Pressure

\[ \frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1} \Rightarrow \frac{p_2 V_2}{p_1 V_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1} \Rightarrow \frac{p_2}{p_1} = \left( \frac{V_1}{V_2} \right)^{\gamma} \Rightarrow p_1 V_1^{\gamma} = p_2 V_2^{\gamma} \]

Let compare the shape of an isotherm to the shape of an adiabat on a pV plot.

Note that the slope of the adiabat is always greater since the heat capacitity ratio, \( \gamma \) is always greater than one.

Adiabatic Internal Energy

\[ dU = dq + dw \quad \Rightarrow \quad dU = dw \quad \Rightarrow \quad \Delta U = -\int p_{ex} \cdot dV \]

Why not \( \Delta U = -nRT \ln \left( \frac{V_2}{V_1} \right) \) for a reversible ideal gas?

- Not necessarily isothermal conditions
- Can’t pull T out of integral

Adiabatic Enthalpy

\[ H = U + pV \quad \Rightarrow \quad dH = dU + d(pV) = dq + dw + p \, dV + v \, dp \]
\[ \Rightarrow \quad dH = -p \, dV + p \, dV + v \, dp \quad \Rightarrow \quad dH = v \, dp \]
Carnot Cycle

We have supposed that entropy is state function. However we have not proven it. We can use a thermodynamic cycle constructed by the French military engineer, Sadi Carnot to demonstrate that entropy is indeed a state function.

We will use Carnot’s inspired choice of closed path to

I. Demonstrate that \( \oint \frac{dq_{rev}}{T} = 0 \) for an ideal gas on Carnot’s path.

II. Demonstrate that \( \oint \frac{dq_{rev}}{T} = 0 \) for an arbitrary substance on Carnot’s path.

III. Demonstrate that \( \oint \frac{dq_{rev}}{T} = 0 \) for an arbitrary substance on an arbitrary path.

Proof I: Ideal gas with Carnot’s path

Step 1. Reversible isothermal expansion at temperature \( T_h \) from point A to point B.

\[
\Delta S_1 = \frac{q_h}{T_h}
\]

Step 2. Reversible adiabatic expansion from point B to point C (or \( T_h \rightarrow T_c \)).

\( \Delta S_2 = 0 \)

Step 3. Reversible isothermal compression at temperature \( T_c \) from point C to point D.

\[
\Delta S_3 = -\frac{q_c}{T_c}
\]

Step 4. Reversible adiabatic compression from point D to point A (or \( T_c \rightarrow T_h \)).

\( \Delta S_4 = 0 \)
For the cycle A → B → C → D → A.

\[ \Delta S_{\text{Total}} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = \Delta S_1 + \Delta S_3 \]

\[ \Delta S_{\text{Total}} = \Delta S_1 + \Delta S_3 = \frac{-w_{\text{rev,1}}}{T_h} + \frac{-w_{\text{rev,3}}}{T_c} = \frac{nRT_h \ln \left( \frac{V_B}{V_A} \right)}{T_h} + \frac{nRT_c \ln \left( \frac{V_D}{V_C} \right)}{T_c} = nR \ln \left( \frac{V_B}{V_A} \right) + nR \ln \left( \frac{V_D}{V_C} \right) = nR \ln \left( \frac{V_B V_D}{V_A V_C} \right) \]

Recall a thermodynamic expression for adiabatic expansions: \( T_2 V_2^{γ-1} = T_1 V_1^{γ-1} \)

\[ T_2 V_2^{γ-1} = T_1 V_1^{γ-1} \Rightarrow T_h V_A^{γ-1} = T_c V_D^{γ-1} \quad \text{and} \quad T_h V_B^{γ-1} = T_c V_C^{γ-1} \]

\[ \Rightarrow \frac{T_h}{T_c} = \frac{V_D^{γ-1}}{V_A^{γ-1}} \quad \text{and} \quad \frac{T_h}{T_c} = \frac{V_C^{γ-1}}{V_B^{γ-1}} \Rightarrow \frac{V_D}{V_A} = \frac{V_C}{V_B} \Rightarrow V_B V_D = V_A V_C \]

\[ V_B V_D = V_A V_C \Rightarrow \Delta S_{\text{Total}} = nR \ln \left( \frac{V_B V_D}{V_A V_C} \right) = nR \ln \left( \frac{V_A V_C}{V_A V_C} \right) = nR \ln (1) = 0 \]

**End of Proof 1.**

**Efficiency of Heat Engines**

Definition: efficiency - \( \varepsilon \)

\[ \varepsilon = \frac{|w|}{|q_h|} \]

The efficiency of heat engine in terms of the heat bath temperatures can be found with the following derivation.

\[ \varepsilon = \frac{|w|}{|q_{\text{out}}|} = \frac{|q_{\text{out}}| - |q_{\text{in}}|}{|q_{\text{out}}|} = 1 - \frac{|q_{\text{in}}|}{|q_{\text{out}}|} \]

\[ q_{\text{out}} = -nRT \ln \left( \frac{V_B}{V_A} \right) \]

\[ w = |q_{\text{out}}| - |q_{\text{in}}| = -nRT_h \ln \left( \frac{V_B}{V_A} \right) - nRT_c \ln \left( \frac{V_D}{V_C} \right) = -nRT_h \ln \left( \frac{V_B}{V_A} \right) - nRT_c \ln \left( \frac{V_A}{V_B} \right) \]

\[ = -nRT_h \ln \left( \frac{V_B}{V_A} \right) + nRT_c \ln \left( \frac{V_B}{V_A} \right) = -nR (T_h - T_c) \ln \left( \frac{V_B}{V_A} \right) \]
\[ \varepsilon = \frac{|w|}{q_{out}} = -nR \left(T_h - T_c\right) \ln \left(\frac{V_B}{V_A}\right) = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h} \]

Example: An engine using superheated steam at 550 °C has heat transferring to a thermal sink at 100 °C. What is the maximum efficiency of the engine?

\[ \varepsilon = 1 - \frac{T_c}{T_h} = 1 - \frac{373 \text{ K}}{823 \text{ K}} = 1 - 0.453 = 0.547 \]

Therefore the maximum efficiency of the engine is 54.7%. 45.3% of the energy must be wasted due to the second law of thermodynamics.

Example: If an internal combustion engine cycles between 3200 K and 1400 K, what is its maximum efficiency?

\[ \varepsilon = 1 - \frac{T_c}{T_h} = 1 - \frac{1400 \text{ K}}{3200 \text{ K}} = 1 - 0.44 = 0.56 \]

Thus the maximum efficiency is 56%. In reality the efficiency is more like 25%.

Example: a) If a heat engine has a temperature of 800 K during the hot part of its cycle, at what temperature must the heat sink be to have 95% efficiency?

\[ \varepsilon = 1 - \frac{T_c}{T_h} \Rightarrow \varepsilon - 1 = -\frac{T_c}{T_h} \Rightarrow T_c = T_h (1 - \varepsilon) = 800 \text{ K} (1 - 0.95) = 40 \text{ K} \]

a) At what temperature must the heat sink be to have 100% efficiency?

\[ T_c = T_h (1 - \varepsilon) = 800 \text{ K} (1 - 1) = 0 \text{ K} \]

Thus the only time a heat engine can be 100% efficient is if we can cool our engine to absolute zero. Shortly we’ll see that we can’t cool our engine that far.
We will soon show that two engines operating reversibly between two temperatures, $T_h$ and $T_c$ must have the same efficiency.

Recall Kelvin’s statement of the 2nd Law: No process exists that has the sole result of converting heat to work.

**Proof II  Carnot’s cycle with an arbitrary substance**

We prove that the entropy change of an arbitrary substance going through Carnot’s cycle is zero by proving Carnot’s Theorem below.

**Carnot’s Theorem:** Efficiencies of reversible processes operating between $T_h$ and $T_c$ must be the same regardless of whether the working substance is an ideal or a real gas.

Let us assume that we have two different engines, A and B, operating between the same $T_h$ and $T_c$ and that the two engines have different efficiencies. (We will work toward showing an obvious contradiction that will demonstrate that this initial assumption is false.)

Furthermore let us assume that the efficiency of engine A is higher than efficiency of engine B.
Engine B is not able to perform as much work as Engine A. To make Engine B perform as much work as Engine A, we can increase the size of Engine B (by using more of the working substance).

(Careful: Temperatures $T_h$ and $T_c$ remain the same. Do not let second graphic deceive you.)

At this point, let us run Engine B in reverse and couple it to Engine A, so that Engine B releases heat to the heat bath at $T_h$ and absorbs heat at the heat bath at $T_c$.

During each cycle, the more efficient Engine A absorbs $q_{out}$ at $T_h$ and emits $-q_{in}$ at $T_c$. The less efficient engine B, (going backwards), is emitting heat $-q_{out}'$ at $T_h$ and absorbing heat $q_{out}'$ at $T_c$.

The work performed by Engine A equals the work performed by Engine B.

$$|q_{out} - q_{in}| = |q_{out}' - q_{in}'|$$

However, the efficiency of Engine A is greater than Engine B.

$$\varepsilon > \varepsilon' \quad \Rightarrow \quad \frac{|w|}{q_{out}} > \frac{|w'|}{q_{out}'} \quad \Rightarrow \quad \frac{|q_{out} - q_{in}|}{|q_{out}|} > \frac{|q_{out}' - q_{in}'|}{|q_{out}'|}$$

Since the work (the numerator) is equal on both sides of the inequality,

$$\frac{|q_{out} - q_{in}|}{|q_{out}|} > \frac{|q_{out}' - q_{in}'|}{|q_{out}'|} \quad \Rightarrow \quad \frac{1}{|q_{out}|} > \frac{1}{|q_{out}'|} \quad \Rightarrow \quad |q_{out}'| > |q_{out}|$$
But also using the same inequality,
\[
\frac{|q_{\text{out}}| - |q_{\text{in}}|}{|q_{\text{out}}|} > \frac{|q'_{\text{out}}| - |q'_{\text{in}}|}{|q'_{\text{out}}|} \Rightarrow 1 - \frac{|q_{\text{in}}|}{|q_{\text{out}}|} > 1 - \frac{|q'_{\text{in}}|}{|q'_{\text{out}}|} \Rightarrow \frac{|q_{\text{in}}|}{|q_{\text{out}}|} < \frac{|q'_{\text{in}}|}{|q'_{\text{out}}|}
\]

If under any conditions, \( |q'_{\text{out}}| > |q_{\text{out}}| \), then the equality above can be rewritten as
\[
|q_{\text{in}}| |q'_{\text{out}}| < |q'_{\text{in}}| |q_{\text{out}}| \Rightarrow |q_{\text{in}}| < |q'_{\text{in}}|
\]

The inequality, \( |q'_{\text{out}}| > |q_{\text{out}}| \), implies that the heat emitted by engine B is greater than the heat absorbed by engine A.

The inequality, \( |q_{\text{in}}| < |q'_{\text{in}}| \), implies that the heat emitted by engine A is greater than the heat absorbed by engine B.

Both the above statements imply that as the coupled engine cycle, heat is being transferred from the low temperature bath to the high temperature bath. That is thermal energy is spontaneously flowing from cold to hot. This heat flow violates what we know about heat flow (Fourier’s Law of Heat Conduction).

Therefore the initial assumption that Engine A and Engine B can have different efficiencies while cycling between the same temperatures must be false.

**Thus the efficiency of a heat engine depends on temperatures it cycles between and not on the nature of the working substance in the engines.**

**Continuing with proof II.**

\[
\varepsilon = 1 - \frac{|q_c|}{|q_h|} = 1 - \frac{T_c}{T_h} \Rightarrow \frac{|q_c|}{|q_h|} = \frac{T_c}{T_h} \Rightarrow \frac{|q_h|}{T_h} = \frac{|q_c|}{T_c}
\]

From the Carnot cycle
\[
\oint dS = \frac{|q_h|}{T_h} - \frac{|q_c|}{T_c} = 0
\]

**End of proof II.**
Proof III  Arbitrary cycle with an arbitrary substance

The proof for an arbitrary cycle is rather ingenious.

1. Tile a chosen arbitrary closed path with Carnot cycles.

2. Make Carnot cycles smaller to fit as many as possible within the boundary enclosed by the path.

3. As the Carnot cycle get infinitesimally small, the entire boundary is contributing to at least one Carnot cycle on its interior.

4. The entropies of all the Carnot cycle paths in the interior of the boundary cancel each other.

5. The total entropy of all of the Carnot cycles is zero; therefore, the entropy for the arbitrary closed path is zero.
Entropy as a Statistical Measure

Classical Thermodynamic View of Entropy

_Clausius’ definition of entropy_

\[
\frac{dS}{T} = \frac{dq_{rev}}{T}
\]

\(dq\) is an inexact differential \(\Rightarrow\) line integral of \(dq\) depends on path

\(1/T\) is an integrating factor so that \(dS\) is an exact differential \(\Rightarrow\) line integral of \(dS\) is independent of path \(\Rightarrow S\) is a state function.

Statistical View of Entropy

System evolves so that it can occupy a greater number of energy states.

_Boltzmann’s definition of entropy_

\[
S = k \ln \omega
\]

where \(\omega\) is the total number of possible arrangement of states for a given energy.

- Note if \(\omega = 1\), then \(S = 0\).

\(k\) – Boltzmann’s constant = \(1.3806503 \times 10^{-23}\) J/K

\(k\) is a fundamental constant of nature and has a simple relationship with the Ideal Gas Constant, \(R\).

\[
R = k \cdot N_A
\]

where \(N_A\) is Avogadro’s number.

Equivalence of Views

To rigorously demonstrate that the two views are equivalent takes a lot of sophisticated mathematical machinery. We’ll avoid such sophistication in this class.

Let us at least demonstrate that the views are equivalent for the simple system of the isothermal expansion for an ideal gas.

_Thermodynamic View (19th century)_

Consider the entropy change for an isothermal expansion of an ideal gas

\[
\Delta S = \int_{i}^{f} \frac{dq_{rev}}{T} = \frac{1}{T} \int_{i}^{f} dq_{rev} \quad \Rightarrow \quad \Delta S = \frac{q_{rev}}{T}
\]
For an ideal gas, the molar internal energy is, \( \overline{U} = \frac{3}{2}RT \).

Therefore for an isothermal process,

\[
\Delta T = 0 \quad \Rightarrow \quad \Delta U = 0 \quad \Rightarrow \quad \Delta U = q_{\text{rev}} + w_{\text{rev}} \quad \Rightarrow \quad q_{\text{rev}} = -w_{\text{rev}}
\]

\[
w_{\text{rev}} = -\int p_{\text{ex}} \, dV = -\int p \, dV = -\int \frac{nRT}{V} \, dV = -nRT \int \frac{1}{V} \, dV = -nRT \ln \left( \frac{V_f}{V_i} \right)
\]

Thus the entropy for an isothermal expansion of an ideal gas can be written as

\[
\Delta S = \frac{-w_{\text{rev}}}{T} = -\frac{nRT \ln \left( \frac{V_f}{V_i} \right)}{T} = nR \ln \left( \frac{V_f}{V_i} \right)
\]

**Statistical View (20th century)**

Consider \( N \) ideal gas particles in a volume \( V \). The volume that one particle occupies can be considered a peculiar type of density. volume per particle = \( v \).

1. How many places can I put a single gas particle in the volume?

\[
\omega = \frac{V}{v}
\]

2. How many places can I put two gas particles in the volume?

\[
\omega = \left( \frac{V}{v} \right) \left( \frac{V}{v} \right) = \left( \frac{V}{v} \right)^2
\]

3. How many places can I put \( N \) gas particles?

\[
\omega = \left( \frac{V}{v} \right) \left( \frac{V}{v} \right) \cdots \left( \frac{V}{v} \right) = \left( \frac{V}{v} \right)^N
\]

Using Boltzmann’s definition, we can calculate the entropy change when we isothermally change the volume.

\[
\Delta S = S_f - S_i = k \ln \omega_f - k \ln \omega_i = k \ln \left( \frac{V_f}{v} \right)^N - k \ln \left( \frac{V_i}{v} \right)^N = Nk \ln \left( \frac{V_f}{V_i} \right) - Nk \ln \left( \frac{V_i}{V_f} \right)
\]

\[
= Nk \ln \left( \frac{V_f}{V_i} \right) = Nk \ln \left( \frac{V_f}{V_i} \right)
\]
Calculation of Entropy Changes

Constant volume entropy changes

\[ \frac{dS}{T} = \frac{\Delta q_{rev}}{T} = \frac{C_v}{T} \Rightarrow \int_{s_i}^{s_f} dS = \int_{T_i}^{T_f} \frac{C_v}{T} \, dT \Rightarrow S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_v}{T} \, dT \]

If \( C_v \) is assumed to be constant over the temperature range from \( T_i \) to \( T_f \),

\[ S(T_f) - S(T_i) = \int_{T_i}^{T_f} \frac{C_v}{T} \, dT = C_v \ln \frac{T_f}{T_i} = C_v \ln \left( \frac{T_f}{T_i} \right) \]

Note that the key step in the calculation is noting how we are going to calculate the reversible heat.

Constant pressure entropy changes

\[ \frac{dS}{T} = \frac{\Delta q_{rev}}{T} = \frac{C_p}{T} \Rightarrow \int_{s_i}^{s_f} dS = \int_{T_i}^{T_f} \frac{C_p}{T} \, dT \Rightarrow S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_p}{T} \, dT \]

If \( C_p \) is assumed to be constant over the temperature range from \( T_i \) to \( T_f \),

\[ S(T_f) - S(T_i) = \int_{T_i}^{T_f} \frac{C_p}{T} \, dT = C_p \ln \frac{T_f}{T_i} = C_p \ln \left( \frac{T_f}{T_i} \right) \]
Example: Calculate the entropy change in tetrahydrofuran from 273 K to 333 K given the following expression for the constant pressure heat capacity:

\[
C_p = 63.393 \text{J/mol} \cdot \text{K} + 0.40257 \text{J/mol} \cdot \text{K}^2 T - 1.2686 \times 10^{-3} \text{J/mol} \cdot \text{K}^3 T^2 \\
+ 1.8275 \times 10^{-6} \text{J/mol} \cdot \text{K}^4 T^3
\]

\[
\Delta S = S(333 \text{K}) - S(273 \text{K}) = \int_{273 \text{K}}^{333 \text{K}} \frac{C_p \,dT}{T}
\]

\[
\Delta S = \int_{273 \text{K}}^{333 \text{K}} \frac{63.393 \text{J/mol} \cdot \text{K} + 0.40257 \text{J/mol} \cdot \text{K}^2 T}{T} \,dT
\]

\[
- \int_{273 \text{K}}^{333 \text{K}} 1.2686 \times 10^{-3} \text{J/mol} \cdot \text{K}^3 T^2 + 1.8275 \times 10^{-6} \text{J/mol} \cdot \text{K}^4 T^3 \,dT
\]

\[
\Delta S = (63.393 \text{J/mol} \cdot \text{K}) \ln \frac{T}{273 \text{K}} + (0.40257 \text{J/mol} \cdot \text{K}^2 T - \left(1.2686 \times 10^{-3} \text{J/mol} \cdot \text{K}^3 T^2 + \frac{1.8275 \times 10^{-6} \text{J/mol} \cdot \text{K}^4 T^3}{T}ight) \Delta S
\]

\[
\Delta S = (63.393 \text{J/mol} \cdot \text{K}) \ln \frac{333 \text{K}}{273 \text{K}} + (0.40257 \text{J/mol} \cdot \text{K}^2 T - 1.2686 \times 10^{-3} \text{J/mol} \cdot \text{K}^3 T^2 + 1.8275 \times 10^{-6} \text{J/mol} \cdot \text{K}^4 T^3 \frac{333 \text{K}}{273 \text{K}} - 273 \text{K})
\]

\[
\Delta S = 12.594 \text{J/mol} \cdot \text{K} + 24.154 \text{J/mol} \cdot \text{K} - 23.063 \text{J/mol} \cdot \text{K} + 10.100 \text{J/mol} \cdot \text{K}
\]

\[
= 23.784 \text{J/mol} \cdot \text{K}
\]

Example: Calculate the entropy change of poly(dimethylsiloxane)-5 from 298 K to 340 K at constant atmospheric pressure.

\[
C_p (\text{EtOH}) = 98.39 + 0.5368(T(\text{K}) - 273.25) \text{J/mol} \cdot \text{K}
\]

The heat capacity depends on temperature, so we must do the integral.

\[
S(340 \text{K}) - S(298 \text{K}) = \int_{298 \text{K}}^{340 \text{K}} \frac{C_p \,dT}{T} = \int_{298 \text{K}}^{340 \text{K}} \frac{[98.39 + 0.5368(T - 273.25)]}{T} \,dT
\]

\[
= \int_{298 \text{K}}^{340 \text{K}} \frac{98.39 - 147.5}{T} \,dT + \int_{298 \text{K}}^{340 \text{K}} 0.5368 \,dT = -49.1 \ln T \frac{340 \text{K}}{298 \text{K}} + 0.5368 T \frac{340 \text{K}}{298 \text{K}}
\]

\[
= -6.47 \text{J/mol} \cdot \text{K} + 22.55 \text{J/mol} \cdot \text{K} = 16.08 \text{J/mol} \cdot \text{K}
\]
Chemical Processes

Standard entropies

Standard entropies are tabulated for substances at 1 bar and 298.15 K. For the elements in their standard state, [Carbon (graphite), O\(_2\) (g), Hg (l), P\(_4\) (s)] ; the standard entropies are not zero in contrast to the standard enthalpies of formation for the elements.

Entropies can be given an absolute reference based on the third law of thermodynamics. Standard enthalpies of the elements can’t be given an absolute reference; therefore, the arbitrary reference of zero is free for us to choose.

Constant volume or constant pressure changes

For a chemical reaction, the standard entropy of the reaction can be calculated using a stoichiometric sum of the standard entropies.

\[
\Delta S_{\text{rxn}} = \sum v_i S^0_i
\]

The temperature dependence of the entropy can be found using the stoichiometric sum of the heat capacity, dividing by the temperature and integrating through the temperature range.

\[
\Delta S_{\text{rxn}} = \sum v_i S^0_i + \sum v_i \int_{298}^T \frac{C^0_{p,i}}{T} \, dT
\]
Phase transitions

Phase transitions occur at constant temperature and pressure. (much more about this later in the course) Thus we can relate the entropy change of a phase transition to its enthalpy change.

\[
\Delta S = \int \frac{dq_{rev}}{T} \quad \Delta T = 0 \quad \sum S = \frac{q_{rev}}{T} \quad \Delta p = 0 \quad \Delta S = \frac{\Delta H}{T}.
\]

Plot of the heat capacity and entropy as temperature of a substance increases from zero to the gaseous region.

Items to note from plots

1. The heat capacities and the entropies are discontinuous at the phase transitions temperatures.
2. The heat capacities for solids generally increase with increasing temperature.
3. \( C_p/T \) near absolute zero has a form of \( C_p/T = aT^2 \).
4. The heat capacities for liquids and gases are roughly constant over large temperature regions so that \( C_p/T \) steadily decreases with temperature.
5. The entropy of a substance always increases with increasing temperature.
Trouton’s rule

As an undergraduate Frederick Trouton, spending an afternoon playing with thermodynamics tables, found that the molar entropy of vaporization for most substances is very close to the value of 87 J/mol·K.

$$\Delta \tilde{S}_{vap} \approx \frac{87 J}{\text{mol} \cdot \text{K}}$$

Stated another way, Trouton’s rule shows that for most substances, the difference between the entropy of the liquid phase and the entropy of the gaseous phase is the same. Important exceptions to Trouton’s rule include hydrogen bonded substances, like H₂O and substances with molecules that have low moments of inertia (low rotational energies) like CH₄.

The Third Law of Thermodynamics

Statement

If the entropy of every element in its most stable state at T = 0 K is taken to be zero, then every substance has a positive entropy with may go to zero as T → 0 K, and does so for all perfect crystalline substances including compounds.

Nernst Heat Theorem

Consider a process that takes place at some temperature T with some entropy change $\Delta S(T)$. Then $\Delta S(T) \to 0$ as $T \to 0$.

A consequence of the third law is that absolute zero will never be achieved (thus the name, absolute zero).

Another consequence is that a heat engine’s has 100% efficiency only if it can be cooled to absolute zero.

$$\varepsilon = 1 - \frac{|q_c|}{|q_h|} = 1 - \frac{T_c}{T_h} \quad \Rightarrow \quad \varepsilon (T_c \to 0) = \lim_{T_c \to 0} \left(1 - \frac{T_c}{T_h}\right) = 1$$
Third law entropy calculations

For a substance in the gaseous phase, the third law (absolute) entropy can be calculated using several steps.

\[
S(T) = S(0) + \int_0^{T_{m⁢t}} \frac{dq_{rev}}{T} + \frac{\Delta H_{\text{melting}}}{T_{m⁢t}} + \int_{T_{m⁢t}}^{T_{b⁢o⁢i⁢l}} \frac{dq_{rev}}{T} + \frac{\Delta H_{\text{boiling}}}{T_{b⁢o⁢i⁢l}} + \int_{T_{b⁢o⁢i⁢l}}^{T} \frac{dq_{rev}}{T}
\]

For a constant volume process, the calculation is messy since the volume of a substance almost always changes during a phase transition. However assuming constant pressure the calculation is tractable.

\[
S(T) = S(0) + \int_0^{T_{m⁢t}} \frac{C_p(\text{solid})}{T} \, dT + \frac{\Delta H_{\text{melting}}}{T_{m⁢t}} + \int_{T_{m⁢t}}^{T_{b⁢o⁢i⁢l}} \frac{C_p(\text{liquid})}{T} \, dT + \frac{\Delta H_{\text{boiling}}}{T_{b⁢o⁢i⁢l}} + \int_{T_{b⁢o⁢i⁢l}}^{T} \frac{C_p(\text{gas})}{T} \, dT
\]

The only other issue to consider is the technological problem that we are not able to measure the heat capacities of substances with temperature close to absolute zero. We have to appeal to theory rather than experiment to find such low temperature entropies.

**Einstein-Debye law**

\[
C_v = \frac{12\pi^4}{5} \, \frac{R}{T^3} \left( \frac{T}{\Theta_D} \right)^3 = aT^3
\]

where \(\Theta_D\) is the Debye temperature of a material. The Debye temperature is a characteristic of a material that depends on the different modes in which the atoms in a solid lattice vibrate. The vibrational modes depend on the particulars of the bonding (metallic or intermolecular) thus each substance has its own Debye temperature.

Below is a short table of Debye temperatures.

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>426 K</td>
<td>Pb</td>
<td>96 K</td>
<td>Sn (white)</td>
<td>195 K</td>
</tr>
<tr>
<td>Cd</td>
<td>186 K</td>
<td>α - Mn</td>
<td>476 K</td>
<td>Ti</td>
<td>420 K</td>
</tr>
<tr>
<td>Cr</td>
<td>610 K</td>
<td>Ni</td>
<td>440 K</td>
<td>W</td>
<td>405 K</td>
</tr>
<tr>
<td>Cu</td>
<td>344.5 K</td>
<td>Pt</td>
<td>240 K</td>
<td>Zn</td>
<td>300 K</td>
</tr>
<tr>
<td>Au</td>
<td>165 K</td>
<td>Si</td>
<td>640 K</td>
<td>Diamond</td>
<td>2200 K</td>
</tr>
<tr>
<td>α - Fe</td>
<td>464 K</td>
<td>Ag</td>
<td>225 K</td>
<td>Ice</td>
<td>192 K</td>
</tr>
</tbody>
</table>

The Einstein-Debye model deviates from experiment at high temperatures; however, at low temperatures (< 20 K), the theory gives an excellent approximation.
Thus a general third law entropy calculation can be completed as follows.

\[ S(T) = S(0) + \int_{0}^{T_{\text{melt}}} \frac{aT}{T} \, dT + \int_{T_{\text{melt}}}^{T_{\text{boil}}} \frac{C_p(\text{solid})}{T} \, dT + \int_{T_{\text{boil}}}^{T} \frac{C_p(\text{gas})}{T} \, dT \]

Note that because of Nernst’s heat theorem, \( S(0) \) for all substances is zero.

Free Energy and the 2\textsuperscript{nd} Law

The 2\textsuperscript{nd} Law under constant volume conditions

\[ dU = dq, \quad \text{since} \quad dw = 0 \quad \text{for constant volume conditions (assuming no non-pV work)} \]

From the Clausius inequality

\[ dS \geq \frac{dq}{T} \quad \Rightarrow \quad dS - \frac{dq}{T} \geq 0 \quad \Rightarrow \quad dS - \frac{dU}{T} \geq 0 \]

At this stage note that if \( U \) is constant, then \( dS \geq 0 \)
And if \( S \) is constant, then \( dU \leq 0 \)

At this stage it’s convenient to construct a new energy function.

Helmholtz Free Energy – \( A \equiv U - TS \)

Under isothermal conditions, \( dA = dU -TdS \)

Return to the Clausius inequality

\[ dS - \frac{dU}{T} \geq 0 \quad \Rightarrow \quad TdS - dU \geq 0 \quad \Rightarrow \quad dU - TdS \leq 0 \quad \Rightarrow \quad dA \leq 0 \]

Therefore when \( T \) and \( V \) are constant, according to the 2\textsuperscript{nd} law, a system loses Helmholtz free energy spontaneously.
The 2\textsuperscript{nd} Law under constant pressure conditions

For constant pressure conditions, $dH = dq_p$ (assuming no non-pV work)

Using the analogous argument to that used in the constant volume case.

$$dS \geq \frac{dq}{T} \implies dS - \frac{dq}{T} \geq 0 \implies dS - \frac{dH}{T} \geq 0$$

Now construct another new energy function.

**Gibbs Free Energy** – $G \equiv H - TS \equiv U + PV - TS$

Under isothermal conditions, $dG = dH - TdS$

$$dS - \frac{dH}{T} \geq 0 \implies TdS - dH \geq 0 \implies dH - TdS \leq 0 \implies dG \leq 0$$

Therefore when $T$ and $P$ are constant, according to the 2\textsuperscript{nd} law, a system loses Gibbs free energy spontaneously.

**Free Energy and Work**

Reconsider the second law under constant volume conditions.

$$dS \geq \frac{dq}{T} \implies TdS \geq dq \implies TdS \geq dU - dw$$

$$dw \geq dU - TdS \implies dw \geq dA$$

The Helmholtz energy is “free” energy because it permits us to find the maximum amount of work that can be done by a system at constant volume. This maximum work is possible only under reversible conditions.

When the energy that is used to increase the entropy of the universe is subtract from the total energy, the remaining energy is “free” to do work.

Now, reconsider the second law under constant pressure and reversible conditions.

$$dU = dq + dw_{total} \implies dH = dU + d(PV) = dq + dw_{total} + d(PV)$$

$$dG = dH - TdS = dq + dw_{total} + d(pV) - TdS$$

$$= dw_{total} + d(PV)$$

$$= dw_{total} + Vdp + p\,dV$$

$$= dw_{non-pV} + dw_{pV} + Vdp + pdV$$

$$= dw_{non-pV} - pdV + 0 + pdV$$

$$dG = dw_{non-pV}$$

Thus the Gibbs free energy for a reversible process is the maximum non-pV work that is available from a process.
Maxwell’s Relations

From internal energy

In the previous chapters, we thought of the natural thermodynamic variable used to describe the internal energy as volume and temperature; that is, \( U \equiv U(T, V) \), since
\[
dU = dq + dw = C_v dT - pdV.
\]

However with our thermodynamic definition of entropy, we can also write \( dU \) as \( dU = dq + dw = T dS - pdV \). Therefore, we can also consider the internal energy as a function of entropy and temperature. \( U \equiv U(S, V) \).

If \( U \equiv U(S, V) \), then
\[
dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV.
\]
Comparing to \( dU = T dS - pdV \), yields the following relationships.

\[
\left( \frac{\partial U}{\partial S} \right)_V = T \quad \left( \frac{\partial U}{\partial V} \right)_S = -p
\]

\( U \) is also state function; therefore, \( dU \) is an exact differential. If \( dU \) is exact, then the following relationships are true:

\[
\frac{\partial}{\partial V} \left( \frac{\partial U}{\partial S} \right)_V = \frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right)_S \quad \Rightarrow \quad \left( \frac{\partial T}{\partial V} \right)_S = -\left( \frac{\partial p}{\partial S} \right)_V
\]

\[
\left( \frac{\partial T}{\partial V} \right)_S = -\left( \frac{\partial p}{\partial S} \right)_V
\]
is the first of Maxwell’s relations, a set of relationships between thermodynamic partial derivatives that are enormously helpful.

From enthalpy

Reconsider enthalpy,
\[
dH = dU + d(pV) = dq + dw + pdV + V dp
\]
\[
= T dS - pdV + pdV + V dp
\]
\[
= T dS + V dp
\]

Thus \( H \equiv H(S, p) \) and
\[
\left( \frac{\partial H}{\partial S} \right)_p = T \quad \left( \frac{\partial H}{\partial p} \right)_S = V
\]

Since \( H \) is a state function, \( dH \) is exact; therefore, the Maxwell relation is

\[
\frac{\partial}{\partial p} \left( \frac{\partial H}{\partial S} \right)_p = \frac{\partial}{\partial S} \left( \frac{\partial H}{\partial p} \right)_S \quad \Rightarrow \quad \left( \frac{\partial T}{\partial p} \right)_S = -\left( \frac{\partial V}{\partial S} \right)_p
\]
From Helmholtz free energy

Reconsider Helmholtz free energy,
\[ dA = dU - d(TS) = dq + dw - TdS - SdT \]
\[ = TdS - pdV - TdS - SdT \]
\[ = -pdV - SdT \]

Thus \( A \equiv A(V, T) \) and
\[ \left( \frac{\partial A}{\partial V} \right)_T = -p \]
\[ \left( \frac{\partial A}{\partial T} \right)_V = -S \]

Since \( A \) is a state function, \( dA \) is exact; therefore, the Maxwell relation is
\[ \frac{\partial}{\partial T} \left( \frac{\partial A}{\partial V} \right)_T = \frac{\partial}{\partial V} \left( \frac{\partial A}{\partial T} \right)_V \Rightarrow -\left( \frac{\partial p}{\partial T} \right)_V = -\left( \frac{\partial S}{\partial V} \right)_T \]

From Gibbs free energy

Reconsider Gibbs free energy,
\[ dG = dA - pdV - SdT + pdV + Vdp + d(pV) \]
\[ = -SdT +Vdp \]

Thus \( G \equiv G(p, T) \) and
\[ \left( \frac{\partial G}{\partial p} \right)_T = V \]
\[ \left( \frac{\partial G}{\partial T} \right)_p = -S \]

Since \( G \) is a state function, \( dG \) is exact; therefore, the Maxwell relation is
\[ \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial p} \right)_T = \frac{\partial}{\partial p} \left( \frac{\partial G}{\partial T} \right)_p \Rightarrow \left( \frac{\partial V}{\partial T} \right)_p = -\left( \frac{\partial S}{\partial p} \right)_T \]
Pressure Dependence of Gibbs Energy

Reconsider Gibbs free energy, \( dG = -SdT + V\, dp \)

At constant temperature, \( dG = V\, dp \Rightarrow G_f - G_i = \int V\, dp \)

Assume an ideal gas, \( G_f - G_i = \int V\, dp = \int \frac{nRT\, dp}{p} = nRT \int \frac{dp}{p} = nRT \ln \left( \frac{p_f}{p_i} \right) \)

\[ G_f = G_i + nRT \ln \left( \frac{p_f}{p_i} \right) \]

How about assume constant volume, (as in a geological process)

\( dG = V\, dp \Rightarrow G_f - G_i = V \int dp \Rightarrow \Delta G = V \Delta p \)

**Fugacity**

In using the thermodynamic variable pressure thus far, we been assuming that gases are ideal. What about the case where \( \frac{nRT}{V} \neq p \). For a real gas, the reading that a pressure transducer takes is called the **fugacity**. Thus at this point we make the distinction between the measurement that is actually made (the fugacity) and the measurement that would have been made in the gas was ideal (the pressure). This distinction is admittedly confusing.

The roots of the word fugacity mean escape. Thus fugacity is sometimes referred to as an “escaping tendency” of gas. The words fugitive and fugue (melodies chasing each other) have the same root.

Fugacity is related to the pressure via a fugacity coefficient, \( \phi \).

\[ f = \phi \, p \]

For ideal gas, \( \phi \) equal one.

**Thermodynamic equilibrium constant**

Once the necessity of using fugacities in our thermodynamic work become apparent, we can now use them to better define the equilibrium constant.

\[ K = \frac{(f_c/p_0)^c}{(f_d/p_0)^d} \frac{(f_e/p_0)^e}{(f_a/p_0)^a} \frac{(f_b/p_0)^b}{(f_b/p_0)^b} \]
Calculating fugacity coefficients for a real gas

Fugacity coefficients can be calculated theoretically from a particular real gas equation of state or experimentally from compressibility, Z, data.

To see how this is done, we need to be clever in defining the standard state of real gas. We will make the standard state of real gas the state that makes the gas ideal. The most consistent way to make a real gas ideal is to examine the behavior of the gas as the pressure approaches zero.

\[ \lim_{p \to 0} \frac{f}{f_i} = 1 \]

Recall that pressure dependence of the chemical potential was derived from an integral of the volume with respect to pressure.

\[ dG = Vdp \Rightarrow \mu_f - \mu_i = \int_{p_i}^{f} \tilde{V}dp = RT \ln \left( \frac{p_f}{p_i} \right) \]

Now consider the differences between the real gas and the ideal gas.

\[ \int_{p_i}^{f} \left( \tilde{V} - \tilde{V}_{\text{ideal}} \right)dp = RT \ln \left( \frac{f}{f_i} \right) - RT \ln \left( \frac{p_f}{p_i} \right) = RT \ln \left( \frac{f \cdot p_i}{f_i \cdot p_f} \right) = RT \ln \left( \frac{p_i}{p_f} \right) \]

If the initial state in both cases is the standard state, then \( p_i = f_i \).

\[ \int_{p_i}^{f} \left( \tilde{V} - \tilde{V}_{\text{ideal}} \right)dp = RT \ln \left( \frac{f}{f_i} \right) = RT \ln \left( \frac{\phi p_i}{p_f} \right) = RT \ln \phi \]

Thus if we have compressibility data such that \( \tilde{V} = \frac{ZRT}{p} \), then

\[ \int_{p_i}^{f} \left( \frac{ZRT}{p} - \frac{RT}{p} \right)dp = RT \int_{p_i}^{f} \left( \frac{Z-1}{p} \right)dp = RT \ln \phi \]

\[ \int_{p_i}^{f} \left( \frac{Z-1}{p} \right)dp = \ln \phi \]

Let’s find the activity coefficients for van der Waals gas in terms of parameters “a” and “b”.

First let modify the van der Waals equation to get an expression for $\tilde{V}$.

\[
p = \frac{RT}{V-b} + \frac{a}{V^2} = \frac{1}{V}\left(\frac{RT}{1-b/V} + \frac{a}{V}\right)
\]

Now let's use a Maclaurian series to simplify the expression with covolume.

\[
\frac{1}{1-b/V} = \left(1-\frac{b}{V}\right)^{-1} \Rightarrow (1-x)^{-1}
\]

\[
f(x) = f(x_0) + f'(x_0)(x-x_0) + \frac{1}{2}f''(x_0)(x-x_0)^2 + \cdots
\]

\[= (1-x_0)^{-1} - (-1)(1-x_0)^{-2}(x-x_0) + \frac{1}{2}(-2)(-1)(1-x_0)^{-3}(x-x_0)^2 + \cdots
\]

\[= (1-0)^{-1} - (-1)(1-0)^{-2}(x-0) + \frac{1}{2}(-2)(-1)(1-0)^{-3}(x-0)^2 + \cdots
\]

\[= 1 + x + x^2 + \cdots
\]

Thus \[\frac{1}{1-b/V} \approx 1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2 + \cdots\]

Therefore we can rewrite the van der Waals equation as follows:

\[
p = \frac{1}{V}\left(\frac{RT}{1-b/V} + \frac{a}{V}\right) \Rightarrow \tilde{V} = \frac{RT}{p}\left(1 + \frac{b}{RTV}\right) + \frac{a}{RTV}
\]

\[
\int \left(\tilde{V} - \tilde{V}_{\text{ideal}}\right)dp = RT\ln\phi
\]

\[
\int \left(\frac{RT}{p}\left(1 + \frac{b}{RTV}\right) - \frac{RT}{p}\right)dp = RT\ln\phi
\]

\[
\int \left(\frac{1}{p}\left(1 + \frac{b}{RTV}\right) - \frac{1}{p}\right)dp = \ln\phi
\]

\[
\int \left(\frac{1}{p}\left(\frac{b}{RTV}\right)\right)dp = \ln\phi
\]

\[
\int \left(\frac{1}{pV}\left(b + \frac{a}{RT}\right)\right)dp = \int \left(\frac{1}{RT}\left(b + \frac{a}{RT}\right)\right)dp = \ln\phi
\]

\[
\ln\phi = \frac{b}{RT + \left(\frac{a}{RT}\right)^2}\Delta p
\]
Notes on the fugacity coefficient

1. $Z < 1$ for attractive forces, thus $\phi < 1$
2. $Z > 1$ for repulsive forces, thus $\phi > 1$
3. Usually fugacity coefficient decreases with increasing pressure.

Gibbs-Helmholtz Equation

We can use the relationships to find other relationships. For example, let us find a relationship that describes the temperature dependence of the Gibbs free energy.

$$G = H - TS \Rightarrow \frac{G}{T} = \frac{H}{T} - \frac{TS}{T} = \frac{H}{T} - S$$

Now take the derivative of the expression w.r.t. $T$, holding $p$ constant.

$$\left( \frac{\partial}{\partial T} \right)_p \frac{G}{T} = \left( \frac{\partial G}{\partial T} \right)_p \frac{1}{T} - \left( \frac{\partial G}{\partial T} \right)_p \frac{G}{T^2} = \frac{1}{T} \left[ \left( \frac{\partial G}{\partial T} \right)_p - \frac{G}{T} \right] = \frac{1}{T} \left[ -S - \frac{G}{T} \right] = \frac{1}{T} \left[ -\frac{H}{T} \right] = -\frac{H}{T^2}$$

Because $G$, $H$ and $T$ are all state functions, $\left( \frac{\partial}{\partial T} \right)_p \frac{\Delta G}{T} = -\frac{\Delta H}{T^2}$

Refrigeration

Thermodynamic efficiency

Let us consider a reversible refrigeration cycle $\Rightarrow \Delta S = 0$

Recall from the discussion of the Carnot cycle the relationship between heat and temperature.

$$\Delta S = -\frac{|q_c|}{|T_c|} + \frac{|q_h|}{|T_h|} = 0$$

Let us now define a measure of efficiency in a refrigeration cycle known as the coefficient of performance, $c$. (The fraction of cooling that can be done per unit amount of work supplied.)

$$c = \frac{|q_c|}{|w|}$$
Return to the first law of thermodynamics.

\[
|q_c| - |q_h| + |w| = 0 \quad \Rightarrow \quad |w| = |q_h| - |q_c|
\]

\[
c = \frac{|q_c|}{|w|} = \frac{|q_c|}{|q_h| - |q_c|}
\]

\[
\frac{-|q_c|}{|T_c|} + \frac{|q_h|}{|T_h|} = 0 \quad \Rightarrow \quad \frac{|q_c|}{|q_h|} = \frac{|T_c|}{|T_h|}
\]

\[
c = \frac{|q_c|}{|q_h| - |q_c|} = \frac{|T_c|}{|T_h| - |T_c|}
\]

Compare to efficiency of heat engine \( \varepsilon = \frac{|q_h| - |T_c|}{|T_c|} \)

Thus \( c = \frac{1}{\varepsilon} \)

Note that the performance of a refrigerator worsens as \( T \to 0 \) K.

Also note that \( c > c_{rev} \).
Practical problems with refrigeration

Insulation is imperfect. Because thermal energy is constantly leaking into a system; power (energy per time) must be supplied to keep the temperature constant. The leaking is well described by Newton’s law of cooling,

\[
\text{Power} = \frac{dq_c}{dt} = A \left( T_h - T_c \right),
\]

where \( T_h \) is the temperature of the surroundings and \( T_c \) is the temperature of the refrigerator.

The coefficient \( A \) depends on the
a) heat conductivity of the insulator
b) the size of the refrigerator (power is an extensive quantity)
c) shape (surface area) of the refrigerator (\( A \) increases with higher surface area).

The power need to run the refrigerator can be stated as the amount of work supplied per unit time.

\[
P = \frac{d|w|}{dt}
\]

We can relate the power to the cooling via the coefficient of performance.

\[
|w| = \frac{|q_c|}{c}
\]

\[
P = \frac{1}{c} \frac{d|q_c|}{dt} = \frac{1}{c} A \left( T_h - T_c \right) = \left( \frac{T_h - T_c}{T_c} \right) A \left( T_h - T_c \right) = A \left( \frac{T_h - T_c}{T_c} \right)^2
\]

The squared factor means that electrical power usage (for air conditioners) increases exponentially during a heat wave.
Ultralow temperatures (adiabatic demagnetization)

To produce ultra-low temperatures, a multi-step process must be used.

1. Cool systems with many Joule-Thompson expansions (chlorofluorocarbons, argon and helium are some of the refrigerants used). Approximately 4K can be achieved.

2. Liquid helium evaporation to 1K. (Old-fashioned cooling makes a comeback!)

3. Below 1K adiabatic demagnetization is used. (Refrigerant is a gadolinium salt such as Ga$_2$(SO$_4$)$_3 \cdot 8$ H$_2$O or Gd$_5$Si$_2$Ge$_2$.)
   a) Electron spin of gadolinium (8 unpaired e$^-$) starts randomized.
   b) System is placed in an isothermal bath
   c) Adiabatic magnetization: Magnetic field is applied to align electron spin (and reduce entropy and heat capacity).
   d) Bath is removed, sample is isolated
   e) Adiabatic demagnetization: magnetic field is removed. As magnetic field is removed, temperature decreases.
   f) Repeat

4. To get beyond the nK range nuclear adiabatic demagnetization must be used. (Rhodium metal is refrigerant.)

Current world record cold temperature: 100 pK.

Heat pumps

A heat pump is a refrigerator (air conditioner) working in reverse. Thus during operation, the heat pump cools the outside (in winter!) and heats the inside.

\[
c = \frac{|q_c|}{|q_h| - |q_c|} = \frac{|T_c|}{|T_h| - |T_c|}
\]

The coefficient of performance shows that heat pumps are more practical for Florida and not at all for Alaska. (Your house may be chilly during a cold snap in January in Nebraska.)
The Laws of Thermodynamics
- the wiseacre version.

1\textsuperscript{st} Law  You can't win
2\textsuperscript{nd} Law  You can't break even
3\textsuperscript{rd} Law  You can't get out of the game
0\textsuperscript{th} Law  But you do know how to keep score
Summary

Adiabatic Expansions (or Compressions)

\[ \frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1} \Rightarrow \frac{p_1 V_1}{p_2 V_2} = \left( \frac{V_1}{V_2} \right)^{\gamma-1} \Rightarrow \frac{p_1}{p_2} = \left( \frac{V_1}{V_2} \right)^{\gamma} \]

2nd Law of Thermodynamics (irreversible) \[ \Delta S_{\text{universe}} > 0 \]

2nd Law of Thermodynamics (reversible) \[ \Delta S_{\text{total}} = 0 \]

Thermodynamic definition of entropy \[ dS = \frac{dq_{\text{rev}}}{T} \]

Statistical definition of entropy \[ S = k \ln \omega \]

Definition of ideal gas constant \[ R = k \cdot N_A \]

Entropy change of isothermal expansion of ideal gas.

\[ \Delta S = nR \ln \left( \frac{V_f}{V_i} \right) \]

Entropy is a state function

\[ \oint \frac{dq_{\text{rev}}}{T} = 0 \]

Efficiency of a heat engine

\[ \varepsilon = \frac{|w|}{|q_h|} \quad \varepsilon = 1 - \frac{T_c}{T_h} \quad \varepsilon = 1 - \frac{|q_{\text{in}}|}{|q_{\text{out}}|} \]

Carnot’s Theorem

\[ \varepsilon = 1 - \frac{|q_c|}{|q_h|} = 1 - \frac{T_c}{T_h} \Rightarrow \frac{|q_c|}{|q_h|} = \frac{T_c}{T_h} \Rightarrow \frac{|q_h|}{T_h} = \frac{|q_c|}{T_c} \]

Entropy change at constant volume

\[ S(T_f) = S(T_i) + \int_{T_i}^{T_f} C_v dT \]

Entropy change at constant pressure

\[ S(T_f) = S(T_i) + \int_{T_i}^{T_f} C_p dT \]
Entropy change for constant heat capacity

\[ S(T_f) - S(T_i) = C \ln \left( \frac{T_f}{T_i} \right) \]

Entropy change during phase transition

\[ \Delta S_{\text{trans}} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}} \]

Einstein-Debye heat capacity

\[ C_v = aT^3 \]

Coefficient of performance (refrigeration)

\[ c = \frac{|q_c|}{|w|} = \frac{T_c}{|T_i| - |T_c|} \]

Helmholtz Free Energy

\[ A = U - TS \]

Gibbs Free Energy

\[ G = H - TS \]

Natural Variables of Energies

- Internal Energy \( U \equiv U(V, S, n) \)
- Enthalpy \( H \equiv H(p, S, n) \)
- Helmholtz Free Energy \( A \equiv A(V, T, n) \)
- Gibbs Free Energy \( G \equiv G(p, T, n) \)
Gibbsians

\[ dU = T \, dS - p \, dV \]
\[ dH = T \, dS + V \, dp \]
\[ dA = -p \, dV - S \, dT \]
\[ dG = -S \, dT + V \, dp \]

\[
\begin{align*}
\left( \frac{\partial U}{\partial S} \right)_V &= T \\
\left( \frac{\partial U}{\partial V} \right)_S &= -p \\
\left( \frac{\partial H}{\partial S} \right)_P &= T \\
\left( \frac{\partial H}{\partial p} \right)_S &= V \\
\left( \frac{\partial A}{\partial V} \right)_T &= -p \\
\left( \frac{\partial A}{\partial T} \right)_V &= -S \\
\left( \frac{\partial G}{\partial V} \right)_T &= V \\
\left( \frac{\partial G}{\partial T} \right)_P &= -S
\end{align*}
\]

Maxwell’s Relations

\[
\begin{align*}
\left( \frac{\partial T}{\partial V} \right)_S &= -\left( \frac{\partial p}{\partial S} \right)_V \\
\left( \frac{\partial T}{\partial p} \right)_S &= -\left( \frac{\partial V}{\partial S} \right)_P \\
\left( \frac{\partial p}{\partial T} \right)_V &= \left( \frac{\partial S}{\partial V} \right)_T \\
\left( \frac{\partial V}{\partial T} \right)_P &= -\left( \frac{\partial S}{\partial p} \right)_T
\end{align*}
\]

Gibbs-Helmholtz Equation

\[
\begin{align*}
\left( \frac{\partial}{\partial T} \right)_P \frac{G}{T} &= -\frac{H}{T^2} \\
\left( \frac{\partial}{\partial T} \right)_P \Delta G &= -\frac{\Delta H}{T^2}
\end{align*}
\]

Pressure Dependence of Gibbs Free Energy

\[ G_f = G_i + nRT \ln \left( \frac{p_i}{p_f} \right) \]

Fugacity Coefficient

\[ f = \phi \, p \]

Thermodynamic Equilibrium Constant

\[ K = \frac{(f_c/p^0)^c \, (f_d/p^0)^d}{(f_A/p^0)^a \, (f_B/p^0)^b} \]

Calculation of Fugacity Coefficient

\[ \int f \left( \frac{Z-1}{p} \right) dp = \ln \phi \]