- The entropy of a thermally isolated system increases in any irreversible process and is unaltered in a reversible process. This is the principle of increasing entropy.

2nd Law of Thermodynamics

$\Delta S \geq 0$.

- Calculate the change in entropy of water heated from $20°$C to $100°$C on a stove (Pressure is fixed).
- The definition of entropy gives rise to $\Delta S = \int_{T_i}^{T_f} \frac{dQ_R}{T} = \int_{T_i}^{T_f} \frac{C_P dT}{T}$
- Another way to get the solution is applying the central equation: $\Delta S = \int_i^f \frac{dU}{T} + \int_i^f \frac{P}{T}$ dV.
- We know only T_i and T_f and $P_i = P_f$, but not U_i and U_f or V_i and V_f . Therefore we need to expand dU and dV in terms of $f(P, T)$.

- $\Delta S = \int_i^f \frac{\left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP}{T} + \int_i^f \frac{P}{T} \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP\right]$

- The pot is open to atmosphere so the natural choice of path is isobaric $-dP = 0$;

- $\Delta S = \int_{T_i}^{T_f} \frac{\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P}{T} \ dT = \int_{T_i}^{T_f} \frac{\left(\frac{\partial (U+PV)}{\partial T}\right)_P}{T} dT = \int_{T_i}^{T_f} \frac{\left(\frac{\partial H}{\partial T}\right)_P}{T} dT = \int_{T_i}^{T_f} \frac{C_P dT}{T}.$

Example of Entropy calculation - 2

Kinetic Theory of
Gases

Thermodynamics

State Variables

Zeroth law of
thermodynamics

Reversible and
Irreversible
processes

First law of
Thermodynamics

Second law of
Thermodynamics

Entropy

Thermodynamic
Potential

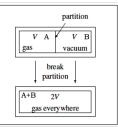Third Law of
Thermodynamics

Phase diagram

- Change in entropy due to electrical work: Consider a current I flowing through a resistor R.
- power delivered is I^2R.
- Suppose the resistor, regarded as the system, completely fills a box with adiabatic walls. The power is dissipated irreversibly in the resistor, which therefore heats up.
- From the 1st law the change in internal energy of the system in time interval Δt is $\Delta U = dQ + dW = I^2R\Delta t$ (assuming the volume is fixed so that no mechanical work is done).
- $dU = C_V dT$.
- Change in temperature: $I^2R\Delta t = \int_{T_i}^{T_f} C_V dT = C_V\Delta T$. This means, $\Delta T = I^2R\Delta t \,/C_V$.
- The change of entropy can be calculated with the central equation, $dS = C_V dT/T \implies \Delta S = \int_{T_i}^{T_f} \frac{C_V dT}{T}$.

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- The Second Law means that the total entropy of an isolated system must increase.
- In statistical physics we expect a system to change from a less probable initial state to a more probable final state. This implies a relationship between probability and entropy.
- Consider the Joule expansion of a large number of atoms, N, of an ideal gas.

- Initially, all the gas is on the left hand side of the container, whereas in the final state the gas has an equal density everywhere.

- $\Delta S = \int S = \int \frac{PdV}{T} = nR \int \frac{dV}{V} = nR \ln(\frac{V_f}{V_i}) = nR\ln(2)$.
- A long time after the partition has been removed and assuming the system is free to explore all possible states available to it (respecting energy conservation), the probability that any one molecule is in A is $1/2$.
- The probability of finding the system in its initial state a long time after the wall has been removed (i.e. the molecules in A) is $\left(\frac{1}{2}\right)^N$.
- Now, define a microstate as a fully specified set of momenta and positions for all molecules. Denote the total number of possible micro-states available with energy E and all the particles in A, to be $\Omega_A \equiv \Omega(N, V_A, E)$.
- for Ω to be countable number, momenta and position states must be quantised.
- denote the total number of states with energy E, N particles, and volume $V_A + V_B$ with the particles located anywhere within volume $V_A + V_B$ as $\Omega_{A+B} \equiv \Omega(N, V_{A+B}, E)$.

- Assuming that all the accessible micro-states are equally likely.
- $\frac{\Omega_A}{\Omega_{A+B}} = \frac{\Omega(N,V,E)}{\Omega(N,2V,E)} = \left(\frac{1}{2}\right)^N$.
- Suppose that there is a relationship between the entropy (S) and the number, Ω, of micro-states available; $S = f(\Omega)$ where f is a function to be determined.
- Entropy is extensive, so if we consider twice as much gas, we should have twice as much entropy, whereas the total number of micro-states available grows much faster, as the product $\Omega_1\Omega_2$. Therefore we require that $f(\Omega_1\Omega_2) = f(\Omega_1) + f(\Omega_2)$
- It may be obvious that only a logarithm can achieve this.
- Differentiating w.r.t Ω_1: $f'(\Omega_1\Omega_2)\,\Omega_2 = f'(\Omega_1)$.
- Differentiating this equation w.r.t Ω_2: $f''(\Omega_1\Omega_2)\,\Omega_1\Omega_2 + f'(\Omega_1\Omega_2) = 0$

- take $x = \Omega_1 \Omega_2$:
- $f''(x)x + f'(x) = \frac{d(xf'(x))}{dx} = 0 \rightarrow f'(x) = k_B/x$ (k_B is an arbitary constant) $\rightarrow f(x) = k_B \ln(x) +$ Constant.
- So if S and Ω are related then the relationship must be of the form $S = k_B \ln(x) + S_0$.
- Set S_0 to zero defines a natural zero for the entropy
- Definition of statistical entropy for fixed energy: $S = k_B \ln(\Omega)$.
- Entropy of a system always increases with increasing temperature, because more states are accessible. Taking logarithm of the expression: $\frac{\Omega_A}{\Omega_{A+B}} = \frac{\Omega(N,V,E)}{\Omega(N,2V,E)} = \left(\frac{1}{2}\right)^N$, it follows $S_{A+B} - S_A = k_B N \ln(2)$.
- S_{A+B} is the statistical entropy of the gas occupying the whole volume (final). S_A is the statistical entropy when the gas is restricted to be in volume V_A (initial). The expression is identical to earlier if we identify $k_B N_A = R$, where $N_A = N/n$ is Avogadro's number and k_B is Boltzmann's constant.

- Let us define a set of N possible states, each with a probability of p_n. By the nature of probability, we must have $\sum_{n=1}^{N} p_n = 1$, with p_n having values between 0 to 1.

- Let us define the entropy of the system according to what has become known as the Gibbs entropy formula: $S = -k_B \sum_{n=1}^{N} p_n \ln p_n$.

- $-\frac{S}{k_B} = \sum_{n=1}^{N} p_n \ln p_n = \sum_{n=1}^{N} \ln p_n^{p_n} = \ln \prod_{n=1}^{N} p_n^{p_n}$

- $\text{Exp} \left(-\frac{S}{k_B}\right) = \prod_{n=1}^{N} p_n^{p_n}$

- Boltzmann defined k_B such that it is equivalent to R/N, N is the avogardo number.

- $k_B = (8.314472 \text{ J/K mole}) / 6.02214179 \times 10^{23}$ molecule/mole $= 1.380650 \times 10^{-23}$ J/K molecule.

Another statement of 2nd Law...

Maxmise Entropy

System+surroundings maximise Entropy S

Compare with mechanical equilibrium

Minimise Energy

System minimises energy

In thermodynamic equilibrium

Minises energy

System minimises energy **Free Energy**

Free energy or Gibbs free energy G, is the energy available in a system to do useful work and is different from the total energy change of a process. Thus, total energy = utilizable energy + non-utilizable energy