Thermodynamics
(Review for Aircraft Propulsion)

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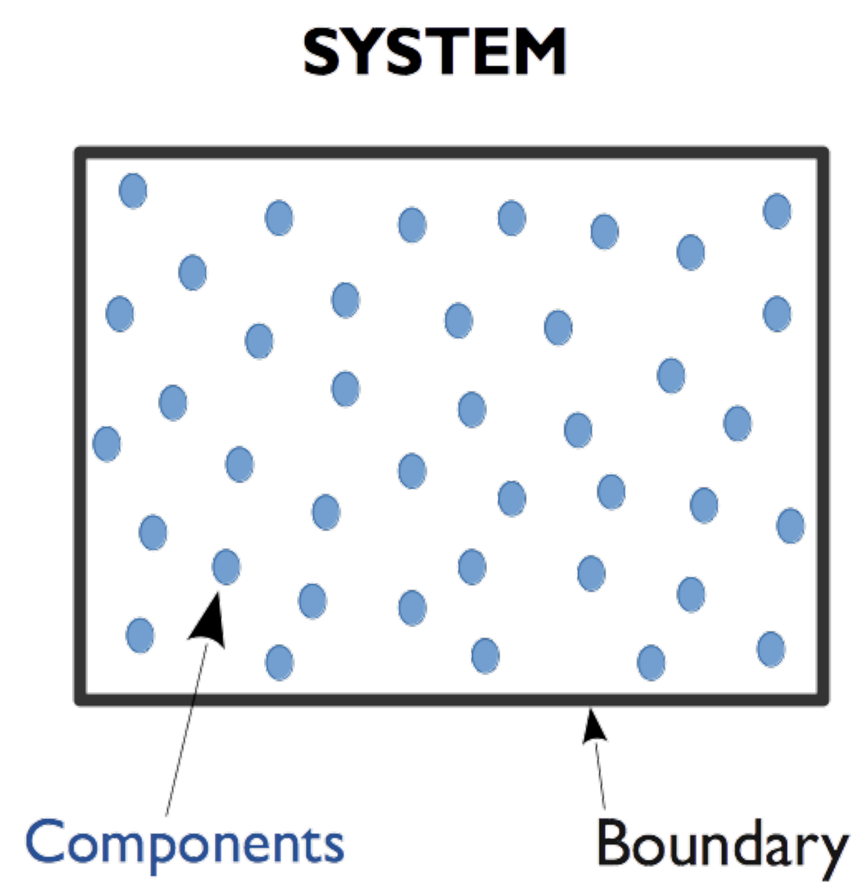
System and its scales

- We can easily observe Macroscopic scales like Volume, Position etc.
- Microscopic scales are not directly visible to us
- Information on Microscopic scales is measured through representative parameters like Composition (moles), Temperature and Pressure



$$\boxed{V, N_1, N_2, \ldots N_n}$$

System and its scales

- **Macroscopic:** The study of mechanics (including elasticity) is the study of one set of surviving coordinates. The subject of electricity (including electrostatics, magnetostatics, and ferromagnetism) is the study of another set of surviving coordinates.

- **Microscopic:** Thermodynamics, in contrast, is concerned with the macroscopic consequences of the myriads of atomic coordinates that, by virtue of the coarseness of macroscopic observations, do not appear explicitly in a macroscopic description of a system.

System and its scales

- **Macroscopic Interaction:** Change in Volume of a gas leads to Work in the form of pdV (Mechanical Work)

- **Microscopic Interaction:** *Energy transfer via hidden atomic modes* is called Heat.

System — State

- Systems tend to settle down to simple states from that of a state of imbalance. Different systems do it at different rates.
- In these terminal ‘simple’ states
  - properties are determined by intrinsic factors and not by previously applied external influences.
  - properties are time independent.
- We call such a state as an **equilibrium state.**

System — State

Postulate I: There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy, volume, and the mole numbers of the chemical components.

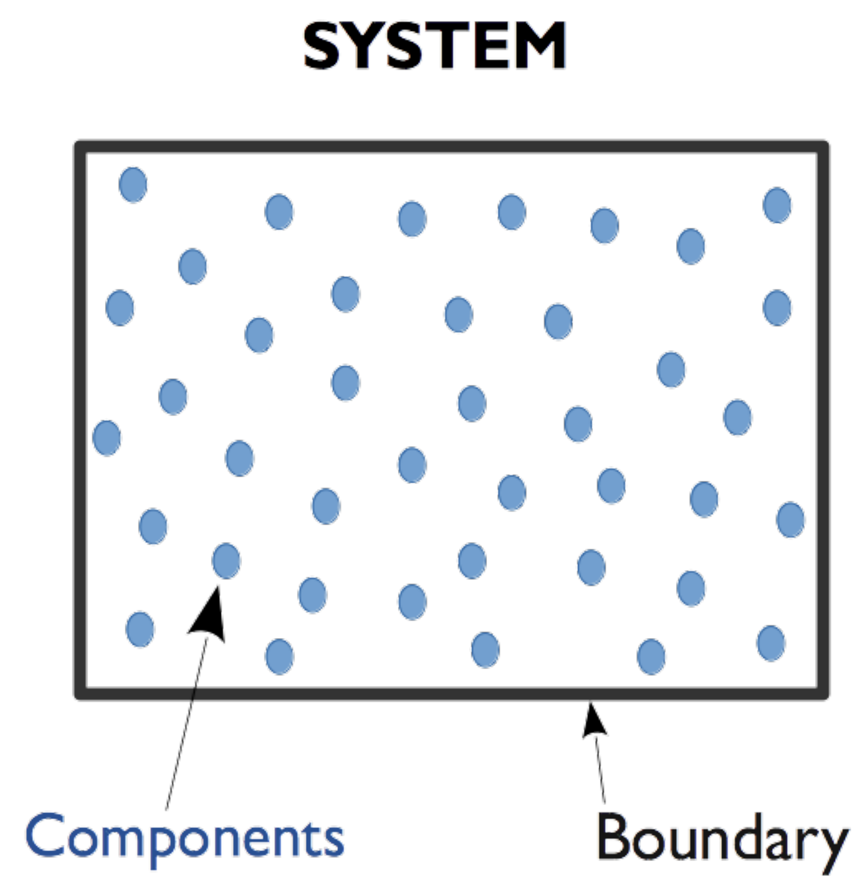
Thermodynamic theory describes such equilibrium states, and processes that connect such states.

System — State — Process

- The state of a system is that which is at equilibrium for the walls/constraints binding the system
- Change/Relaxation of constraints 'shifts' the system to a new equilibrium
- *The single, all encompassing problem of thermodynamics is the determination of the equilibrium state that eventually results after the removal of internal constraints in a closed, composite system.*

Work and Energy

- Count Rumford… Joule
  - Work —> Energy
- Macroscopic Systems have definite and precise energies, subject to a definite conservation principle
  - Internal Energy, E
- The energy is due to microscopic processes
  - When is it definite and precise?
  - Is it measurable?



$$\boxed{V, E, N_1, N_2, \ldots N_n}$$

I Law of Thermodynamics

For any process (involving no net effects external to the system except the displacement of a mass in a gravitational field between specified levels), the magnitude of the mass is fixed by the end states of the system and is independent of the details of the process.

$$-dE = Mgdh \equiv \delta W$$

I Law - Alternate Statement

There exist walls, called **adiabatic**, with the property that the work done in taking an adiabatically enclosed system between two given states is determined entirely by the states independent of all external conditions. The work done is the difference in the internal energy of the two states.

$$-dE = Mgdh \equiv \delta W$$

I Law — Heat Flux

The heat flux to a system in any process (at constant mole numbers) is simply the difference in internal energy between the final and initial states, added to the work done in that process.

$$\delta Q = dE + \delta W \equiv dE + pdV$$

I Law - Directionality

- I Law gives the energy conservation principle for thermodynamic processes
- I Law does not say what process is possible
- Earlier, we said that systems tend to evolve towards an equilibrium state from a state of imbalance.
- I Law does not show any preference for this ‘directionality’ of evolution of systems.

II Law of Thermodynamics

Among all allowed states of a system with given values of energy (E), number of particles (N) and constraints, **one and only one is a stable equilibrium state.** Such a state can be reached from any of the said allowable states <u>without any net effects on the environment</u>.

II Law of Thermodynamics

Postulate II: *There exists a function (called the entropy S) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property: "the values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states."*

$$S = S\left(E, V, N_1, N_2, \ldots N_n\right)$$

II Law of Thermodynamics

Postulate III: *The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous and differentiable and is a monotonically increasing function of energy*.

$$S^{(i)} = S\left(E^{(i)}, V^{(i)}, N_1^{(i)}, N_2^{(i)}, \ldots N_n^{(i)}\right)$$

$$S = \sum_{i=1}^{r} S^{(i)}$$

II Law of Thermodynamics

- Additivity: The entropy of a simple system is a homogenous first-order function of the extensive parameters.

$$S\left(\lambda E, \lambda V, \lambda N_1, \ldots \lambda N_n\right) = \lambda S\left(E, V, N_1, \ldots N_n\right)$$

II Law of Thermodynamics

$$N = \sum_{i=1}^{r} N_i \;\&\; \lambda = \frac{1}{N}$$

$$S\left(\lambda E, \lambda V, \lambda N_1, \ldots \lambda N_n\right) = \lambda S\left(E, V, N_1 \ldots N_n\right)$$

$$s\left(e, v, n_1, \ldots, n_n\right) = \frac{1}{N} S\left(E, V, N_1 \ldots N_n\right)$$

where, s=S/N, e=E/N etc. are the *intensive parameters*, normalized by the total no:of moles in the system.

II Law of Thermodynamics

Monotonicity: Entropy is a single-valued, continuous, and differentiable function of Energy.

$$\left(\frac{\partial S}{\partial E}\right)_{V,N_1,\ldots,N_n} > 0$$

Entropy function can be inverted with respect to the energy.

$$S = S\left(E, V, N_1, \ldots N_n\right)$$

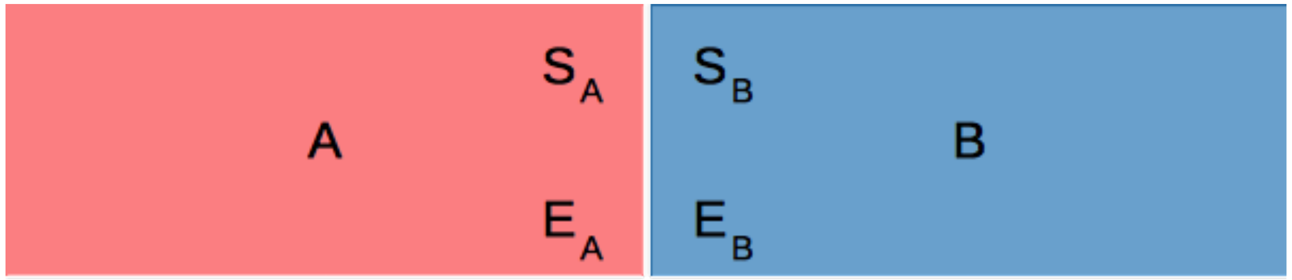
$$E = E\left(S, V, N_1, \ldots N_n\right)$$

Thermodynamic Equilibrium

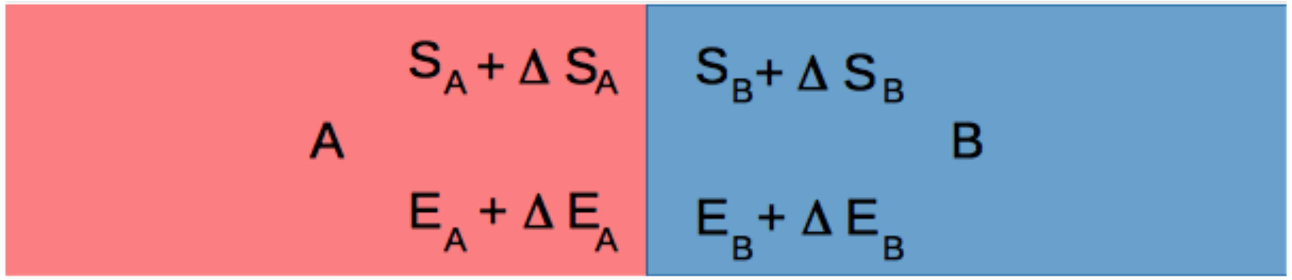
- Thermal
- Mechanical
- Chemical

Thermal Equilibrium

- Two slabs come into diathermal (conducting) contact

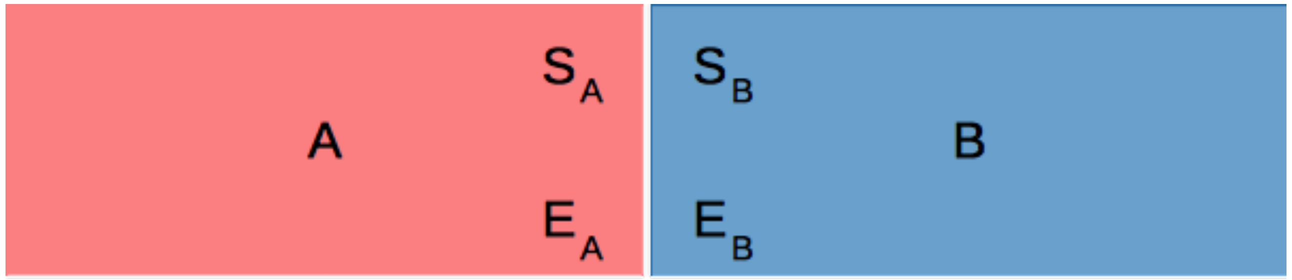


- Energy is Conserved
- When do we have a Stable Equilibrium?

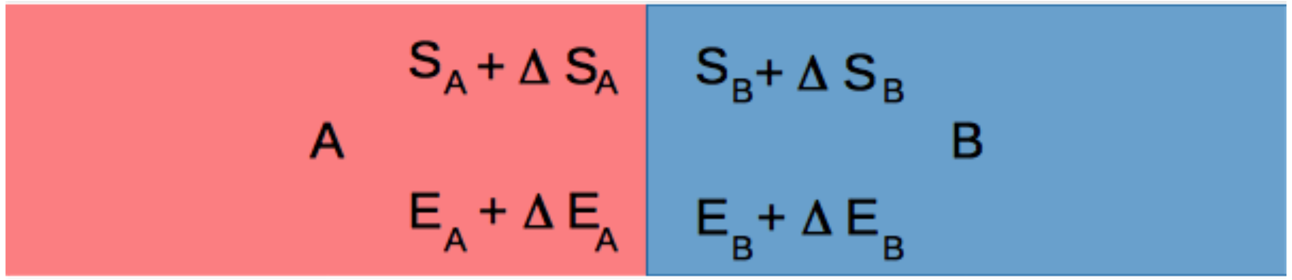


Internal Energy & Temperature

- Heat Flux, When T is not uniform



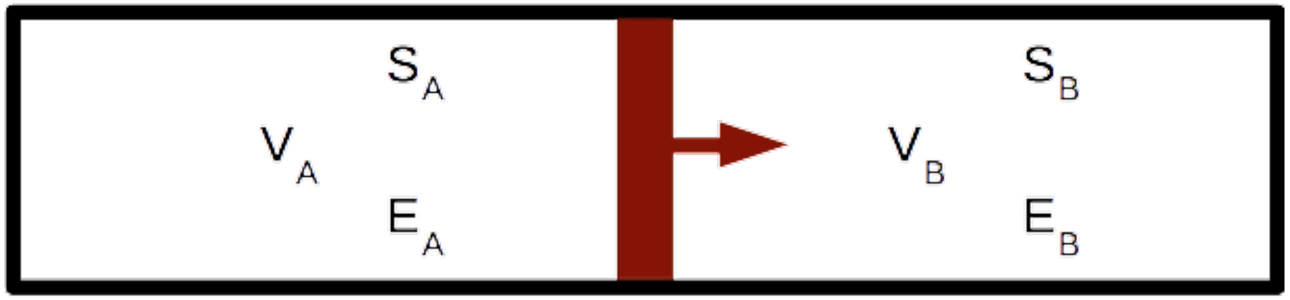
- Heat Flux => Internal Energy Change

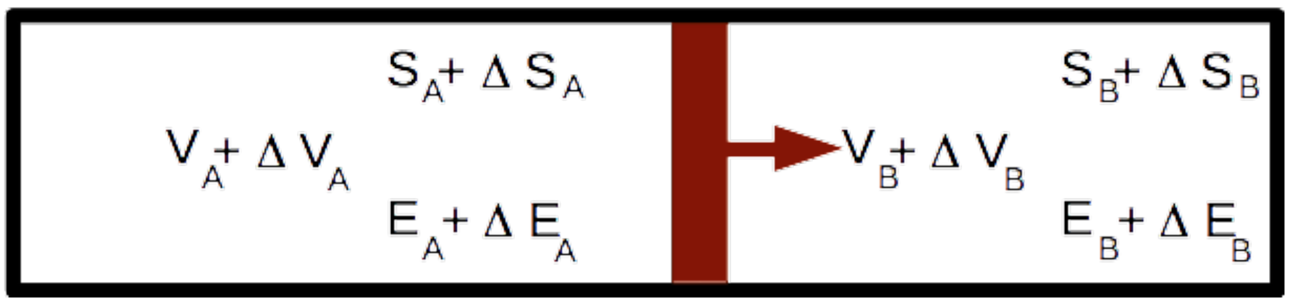


- Temperature, Cv = d E / d T

Mechanical Equilibrium

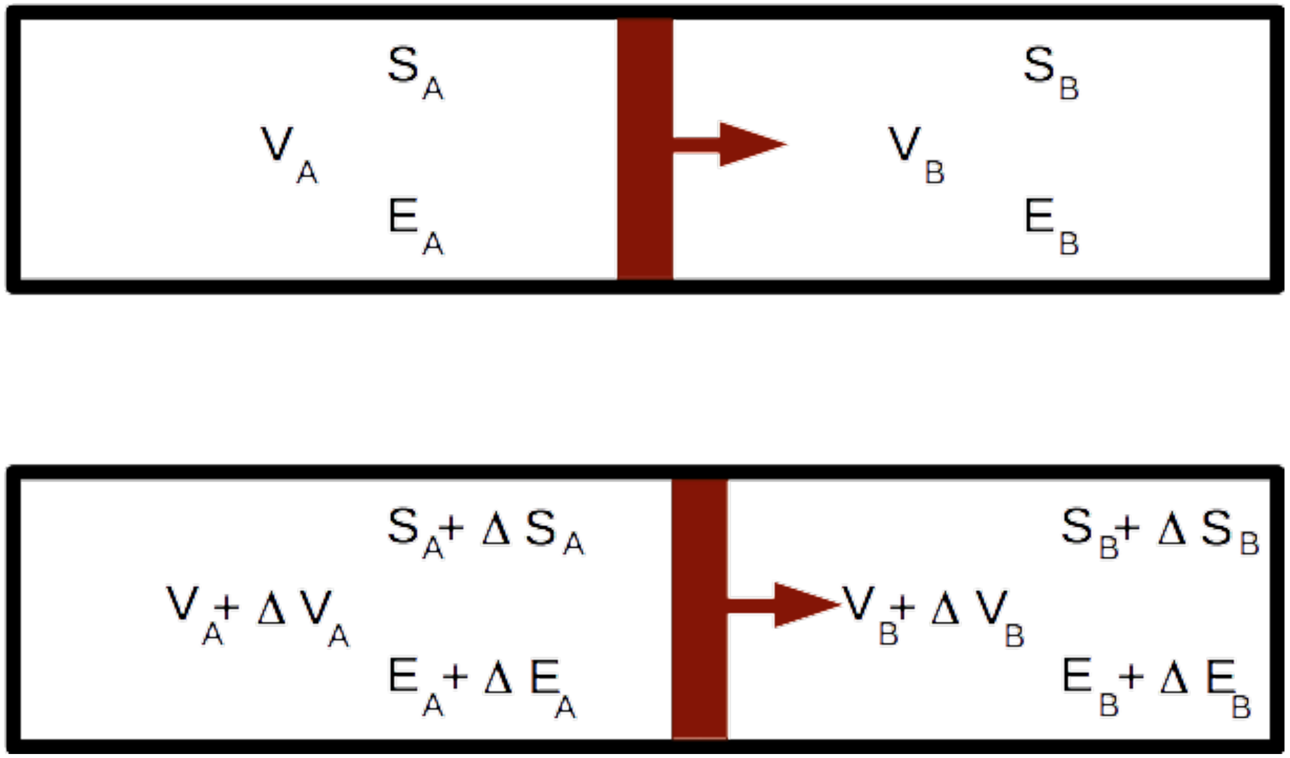
- A stationary piston separating two compartments is allowed to move
- Assume that A and B have the same internal energy
- What is the condition for a stable equilibrium?





Mechanical Equilibrium

- Work done if pressure in A is not the same as pressure in B



Intensive Parameters

$$E = E\left(S, V, N_1, \ldots N_n\right)$$

$$\mathrm{d}E = \left(\frac{\partial E}{\partial S}\right)_{V,N_1,\ldots N_n} \mathrm{d}S + \left(\frac{\partial E}{\partial V}\right)_{S,N_1,\ldots N_n} \mathrm{d}V + \sum_i \left(\frac{\partial E}{\partial N_i}\right)_{S,V,N_1,\ldots N_n} \mathrm{d}N_i$$

$$\left(\frac{\partial E}{\partial S}\right)_{V,N_1,\ldots N_n} = T, \text{ Temperature}$$

$$-\left(\frac{\partial E}{\partial V}\right)_{S,N_1,\ldots N_n} = p, \text{ Pressure}$$

$$\left(\frac{\partial E}{\partial N_i}\right)_{S,V,N_1,\ldots N_n} = \mu_i, \text{ Electro-chemical Potential of ith component}$$

Intensive Parameters

$$\mathrm{d}S = \left(\frac{\partial S}{\partial E}\right)_{V,N_1,\ldots N_n} \mathrm{d}E + \left(\frac{\partial S}{\partial V}\right)_{E,N_1,\ldots N_n} \mathrm{d}V + \sum_i \left(\frac{\partial S}{\partial N_i}\right)_{E,V,N_1,\ldots N_n} \mathrm{d}N_i$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N_1,\ldots N_n} = \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_{E,N_1,\ldots N_n} = \frac{p}{T}$$

$$-\left(\frac{\partial S}{\partial N_i}\right)_{E,V,N_1,\ldots N_n} = \frac{\mu_i}{T}$$

Entropy, Energy & Enthalpy

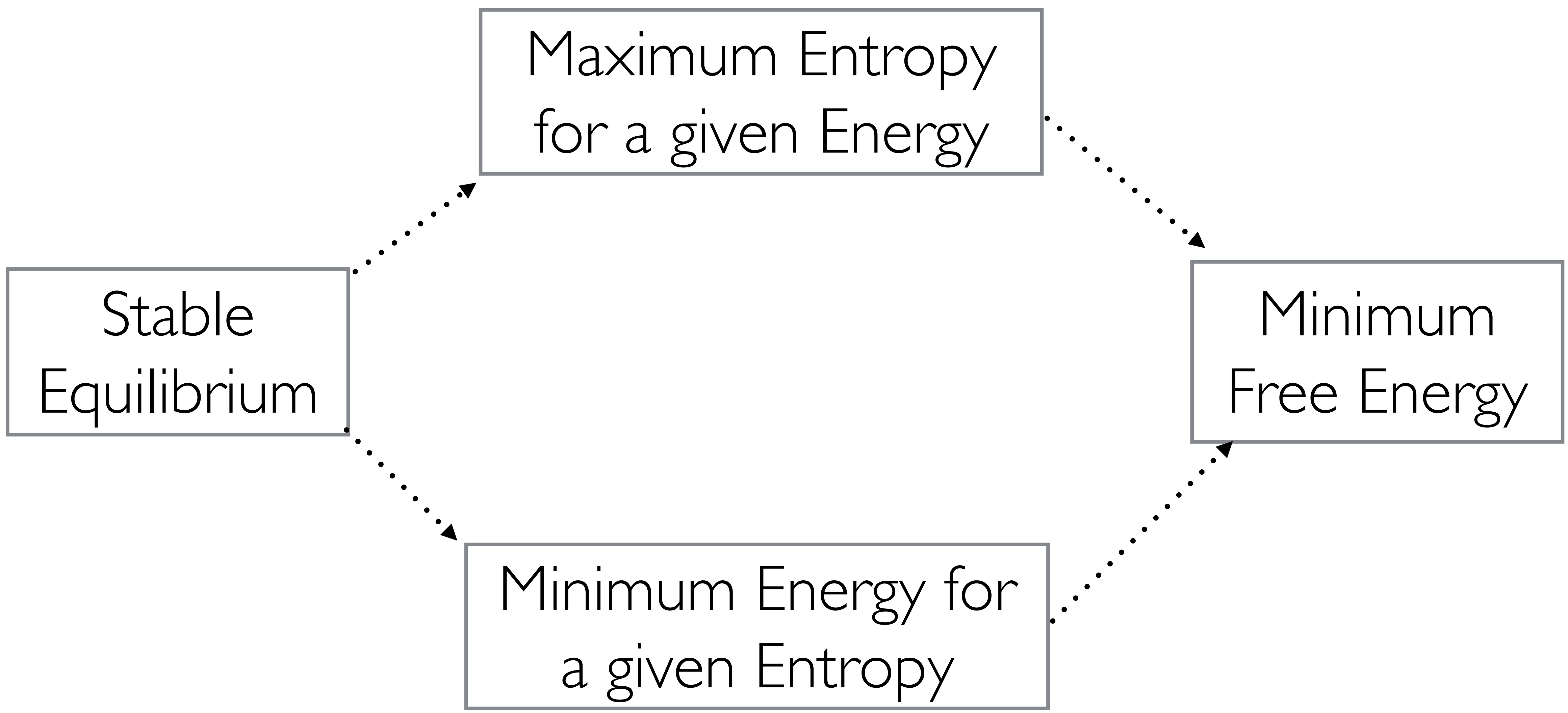
$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E + \frac{p}{T}\mathrm{d}V - \sum_i \frac{\mu_i}{T}\mathrm{d}N_i$$

$$\mathrm{d}E = \underbrace{T\mathrm{d}S}_{\delta Q} - \underbrace{p\mathrm{d}V}_{\delta W} + \sum_i \mu_i \mathrm{d}N_i$$

Define Enthalpy: $H = E + pV$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p + \sum_i \mu_i \mathrm{d}N_i$$

Entropy - Stable Equilibrium



Entropy - Stable Equilibrium

- Entropy is maximized at stable equilibrium
- Energy is conserved
- Minimization of Free Energy — Stable Equilibrium

$$\text{Helmholtz Free Energy: } F = E - TS$$

$$\text{Gibbs Free Energy: } G = H - TS$$

Chemical Equilibrium

- Consider a mixture of species (fuel, oxidiser, products)
- Equilibrium state defined by T, p, V, S, H (or E), G (or F), summed over the contribution due to each species
- For a pure substance, any two of these parameters sufficient to describe the State
- Equilibrium composition can be calculated given any two of these parameters for the mixture
- Temperature dependence of S, H, G tabulated in JANAF tables

Thermodynamic Properties

Nitrogen (N_2) N_2(ref)

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	-8.670	0.	0.	0.
100	29.104	159.811	217.490	-5.768	0.	0.	0.
200	29.107	179.985	194.272	-2.857	0.	0.	0.
250	29.111	186.481	192.088	-1.402	0.	0.	0.
298.15	29.124	191.609	191.609	0.	0.	0.	0.
300	29.125	191.789	191.610	0.054	0.	0.	0.
350	29.165	196.281	191.964	1.511	0.	0.	0.
400	29.249	200.181	192.753	2.971	0.	0.	0.
450	29.387	203.633	193.774	4.437	0.	0.	0.
500	29.580	206.739	194.917	5.911	0.	0.	0.
600	30.110	212.176	197.353	8.894	0.	0.	0.
700	30.754	216.866	199.813	11.937	0.	0.	0.
800	31.433	221.017	202.209	15.046	0.	0.	0.
900	32.090	224.757	204.510	18.223	0.	0.	0.
1000	32.697	228.170	206.708	21.463	0.	0.	0.
1100	33.241	231.313	208.804	24.760	0.	0.	0.
1200	33.723	234.226	210.802	28.109	0.	0.	0.

http://kinetics.nist.gov/janaf/

Chemical Equilibrium

Water (H_2O) $H_2O_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1} mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	-9.904	-238.921	-238.921	INFINITE
100	33.299	152.388	218.534	-6.615	-240.083	-236.584	123.579
200	33.349	175.485	191.896	-3.282	-240.900	-232.766	60.792
298.15	33.590	188.834	188.834	0.	-241.826	-228.582	40.047
300	33.596	189.042	188.835	0.062	-241.844	-228.500	39.785
400	34.262	198.788	190.159	3.452	-242.846	-223.901	29.238
500	35.226	206.534	192.685	6.925	-243.826	-219.051	22.884
600	36.325	213.052	195.550	10.501	-244.758	-214.007	18.631
700	37.495	218.739	198.465	14.192	-245.632	-208.812	15.582
800	38.721	223.825	201.322	18.002	-246.443	-203.496	13.287
900	39.987	228.459	204.084	21.938	-247.185	-198.083	11.496
1000	41.268	232.738	206.738	26.000	-247.857	-192.590	10.060
1100	42.536	236.731	209.285	30.191	-248.460	-187.033	8.881
1200	43.768	240.485	211.730	34.506	-248.997	-181.425	7.897
1300	44.945	244.035	214.080	38.942	-249.473	-175.774	7.063
1400	46.054	247.407	216.341	43.493	-249.894	-170.089	6.346
1500	47.090	250.620	218.520	48.151	-250.265	-164.376	5.724

http://kinetics.nist.gov/janaf/

Configuration Space

- All points correspond to equilibrium states
- ‘Properties’ of a State: S, E, H, V, T, p
- Area under a curve on T-S axes —> Heat Flux
- Area under a curve on p-V axes —> Work Done
- Above true only for quasi-static processes

Process

- Quasi-static process (system moves along equilibrium states)
- e.g., Shocks connect two equilibrium states — 'Jump Conditions'
- Can approximate real process only if entropy is not decreasing
- Real Process (Non-Eq states in between)

Reversible vs Irreversible Process

Slow Free Expansion

- E is unchanged
- Entropy gain, quasi-static, reversible

Rapid Free expansion

- Turbulence, dissipation
- Not quasi-static, irreversible

$\boxed{\text{Slow/Rapid — Relaxation Time}}$

Reference

- Most content from the book by Callen