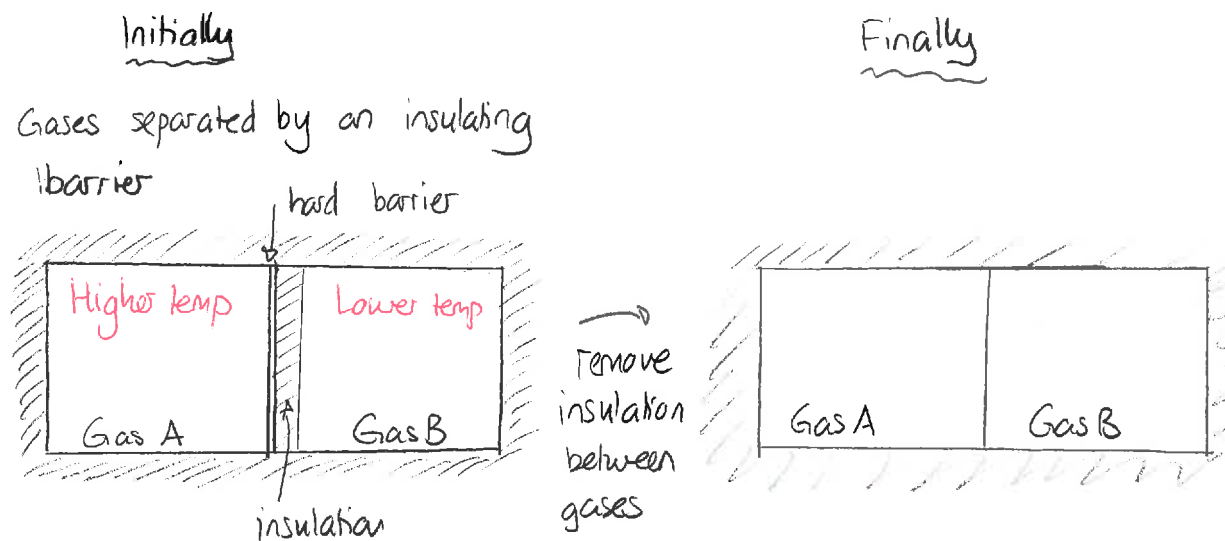Tues: HW by 5pm

☒ Thurs: Read 2.15 , ~~2.16, 2.17~~ 2.17, 2.18

Possible thermodynamic processes

The first law of thermodynamics provides a method for tracking energy and heat flow in processes. There are certain issues that it does not address. Specifically it does not address whether a process could occur or not.

Consider an example where two initially isolated gases are placed in thermal contact.

Initially

Gases separated by an insulating barrier

Finally

During the process will heat flow from Gas A to Gas B. Or will it flow from B to A? Can the first law answer this?

First for system A

$$\Delta E_A = Q_A + W_A$$

and for B

$$\Delta E_B = Q_B + W_B.$$

No work is done on either system. So $W_A = W_B = 0$. Then the total energy of the system $E_A + E_B$ must stay constant. Thus:

$$\Delta E_A + \Delta E_B = 0$$

$$\Rightarrow Q_A + \cancel{W_A} + Q_B + \cancel{W_B} = 0 \qquad \Rightarrow \qquad Q_B = -Q_A$$

This is all that the first law states. We could have $Q_A > 0$ or $Q_A < 0$ and the first law would be satisfied. Thus:

> The first law of thermodynamics is, used alone, not sufficient to describe which processes might occur.

In this example, the first law is still useful. Suppose C_V is independent of temperature for the two systems. Then

$$\delta Q = C_V dT + [\dots] dV$$

$$\Rightarrow \quad \delta Q = C_V dT$$

$$\Rightarrow \quad Q = C_V \Delta T$$

Thus

$$\left. \begin{array}{l} Q_A = C_{V_A} \Delta T_A \\[2mm] Q_B = C_{V_B} \Delta T_B \end{array} \right\} \Rightarrow \qquad C_{V_B} \Delta T_B = - C_{V_A} \Delta T_A$$

So

$$C_{VB}(T_{BF} - T_{Bi}) = -C_{VA}(T_{Af} - T_{Ai})$$

If we know $C_{VA}, C_{VB}, T_{Ai}, T_{Bi}$ then we can use the fact that, at equilibrium $T_{Bf} = T_{Af} = T_f$

$$[C_{VB} + C_{VA}] T_f = C_{VA} T_{Ai} + C_{VB} T_{Bi}$$

$$\Rightarrow \quad T_f = \frac{C_{VA} T_{Ai} + C_{VB} T_{Bi}}{C_{VB} + C_{VA}}$$

This type of conclusion occurs frequently in calorimetry. It uses:

1) energy conservation
2) the first law of thermodynamics   ] essentially energy conservation
3) the fact that at equilibrium the temperatures of the two systems are the same.] ← not energy conservation — something else.
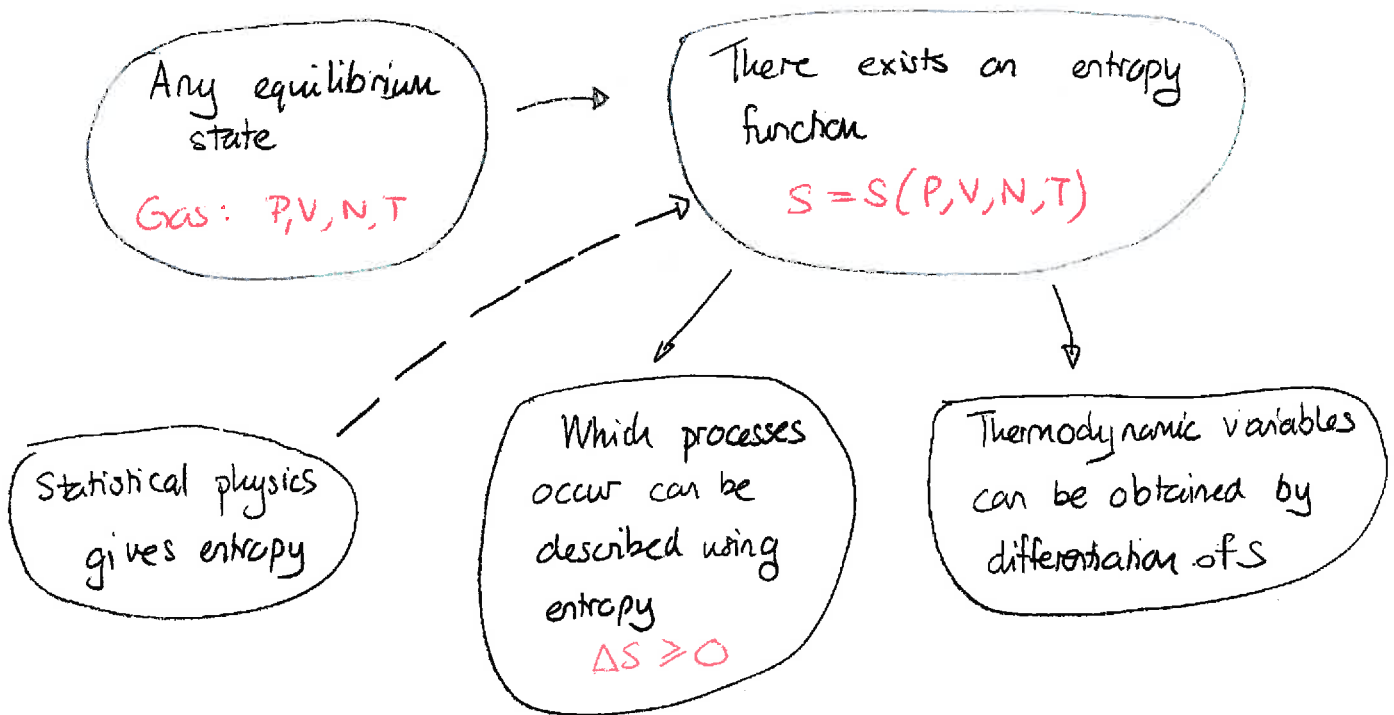
In such situations we always observe that the process satisfies:

1) the heat flows from the high temperature system to the low temperature system.

2) the temperature of the high temp system drops and that of the low temp system rises.

We need another law of thermodynamics that will generate results like this

The Second Law of Thermodynamics and Entropy

The second law of thermodynamics will eventually make the appropriate predictions for the situation of the example There are various versions of this and we will use one that is based on a new macroscopic variable called entropy. We will find the following scheme
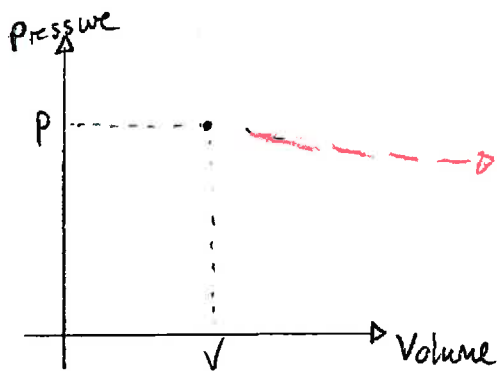
```
┌─────────────────────┐           ┌─────────────────────────┐
│ Any equilibrium     │  ──────→  │ There exists an entropy │
│ state               │           │ function                │
│ Gas: P,V,N,T        │           │ $S = S(P,V,N,T)$        │
└─────────────────────┘           └─────────────────────────┘
```

```
┌─────────────────────┐   ┌─────────────────────┐   ┌─────────────────────────┐
│ Statistical physics │   │ Which processes     │   │ Thermodynamic variables │
│ gives entropy       │   │ occur can be        │   │ can be obtained by      │
│                     │   │ described using     │   │ differentiation of $S$  │
│                     │   │ entropy             │   │                         │
│                     │   │ $\Delta S \geq 0$   │   │                         │
└─────────────────────┘   └─────────────────────┘   └─────────────────────────┘
```

Mathematically the role of entropy starts with

> For any thermodynamic system, there exists a macroscopic quantity, called entropy, and denoted S. This only depends on the state of a system:
>
> $$\text{For a gas} \quad S = S(P,V,T,N,...)$$

In this sense entropy is similar to any other state dependent quantity

For example, for a gas a state can be represented by a point on a PV diagram Then temperature, energy and entropy can be determined from this
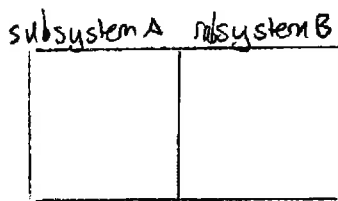
Pressure

P - - - - - - •

Volume

$T = \dfrac{PV}{Nk}$ (Ideal)

$E = \dfrac{3}{2} PV$ (Monoatomic)

$S = ??$ (Entropy)

We will also require that entropy is extensive, which means when two systems are combined the variables add.

subsystem A   subsystem B

	system A	system B	both
particles	N_A	N_B	$N = N_A + N_B$
volume	V_A	V_B	$V = V_A + V_B$
energy	E_A	E_B	$E = E_A + E_B$

Variables that are not extensive are called intensive and examples are pressure, temperature. So it is not generally true that $P = P_A + P_B$

In the case of entropy:

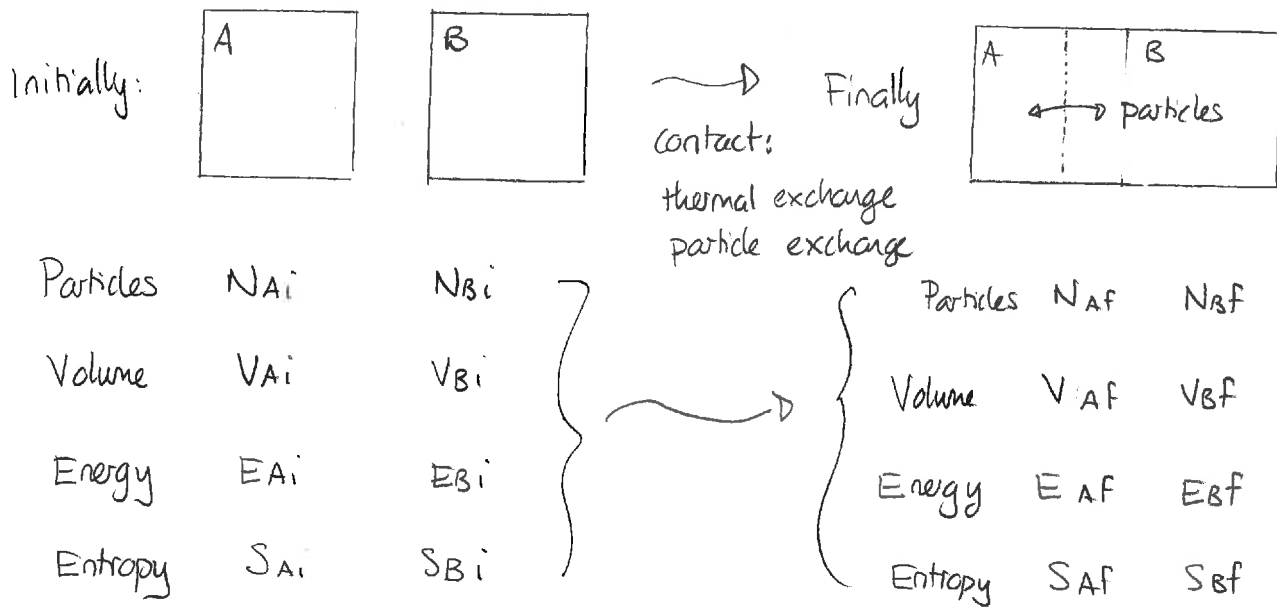If a system consists of two subsystems, A and B then the entropy of the system S satisfies

$$S = S_A + S_B$$

where $S_A = S_A(P_A, T_A, V_A, N_A, ...)$

$S_B = S_B(P_B, T_B, V_B, N_B, ...)$

are the entropies of the subsystems

We now consider two systems in contact with each other and nothing else

Initially:

```
┌─────────┐   ┌─────────┐                                  ┌──────┬──────┐
│ A       │   │ B       │        ↝ →    Finally            │ A    │ B    │
│         │   │         │      contact:                    │   ←──┼─→ particles
│         │   │         │                                  │      ┊      │
└─────────┘   └─────────┘      thermal exchange            └──────┴──────┘
                               particle exchange
```

Particles	N_{Ai}	N_{Bi}
Volume	V_{Ai}	V_{Bi}
Energy	E_{Ai}	E_{Bi}
Entropy	S_{Ai}	S_{Bi}

$$\Big\} \quad \rightsquigarrow \rightarrow \quad \Big\{$$

Particles	N_{Af}	N_{Bf}
Volume	V_{Af}	V_{Bf}
Energy	E_{Af}	E_{Bf}
Entropy	S_{Af}	S_{Bf}

Then we define system totals. For example:

Total particle number $N = N_A + N_B$

Total energy $E = E_A + E_B$

Total entropy $S = S_A + S_B$

We can do this for the initial state and the final state. So we could have

$E_f = E_{Af} + E_{Bf}$ $E_i = E_{Ai} + E_{Bi}$

$S_f = S_{Af} + S_{Bf}$ $S_i = S_{Ai} + S_{Bi}$

How these are related depends partly on the process. For example:

1) no particles lost $\Rightarrow$ $N_f = N_i$ $\Rightarrow$ $N_{Af} + N_{Bf} = N_{Ai} + N_{Bi}$
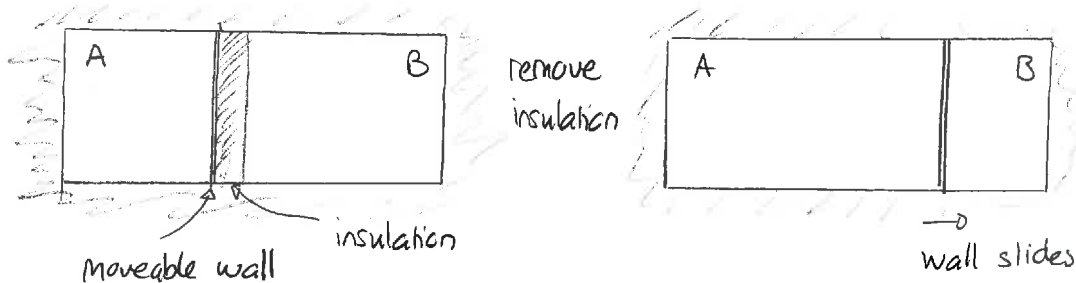
2) no energy lost / no work done by surroundings $\Rightarrow$ $E_{Af} + E_{Bf} = E_{Ai} + E_{Bi}$

Regardless of the process. there will be one requirement. for all processes.

> For any isolated system, the equilibrium state of the system will be such that it attains the maximum entropy possible, subject to all other constraints imposed on the system.

This is the strong form of the second law of thermodynamics.

Consider the law as it might apply to two gases.

remove insulation

moveable wall   insulation   wall slides

Here the constraints would be
* total volume stays constant
* " energy stays constant.

Then the new state for the pair of systems in equilibrium must satisfy: $S_f \geq S_i$. Thus

> For any isolated system, any thermodynamic process must satisfy
> $$\Delta S = S_f - S_i \geq 0$$

A separate definition is:

> A process is reversible $\Longleftrightarrow \Delta S = 0$

We will show that, for example, a free expansion is not reversible.

vol V_{Ai}
energy E_{Ai}
entropy S_{Ai}

vol V_{Bi}
energy E_{Bi}
entropy S_{Bi}

$V_i = V_{Ai} + V_{Bi}$
$V_f = V_{Af} + V_{Bf}$

A?
B?

which states in this region give
$V_{Af} + V_{Bf} = V_{Ai} + V_{Bi}$
$E_{Af} + E_{Bf} = E_{Ai} + E_{Bi}$
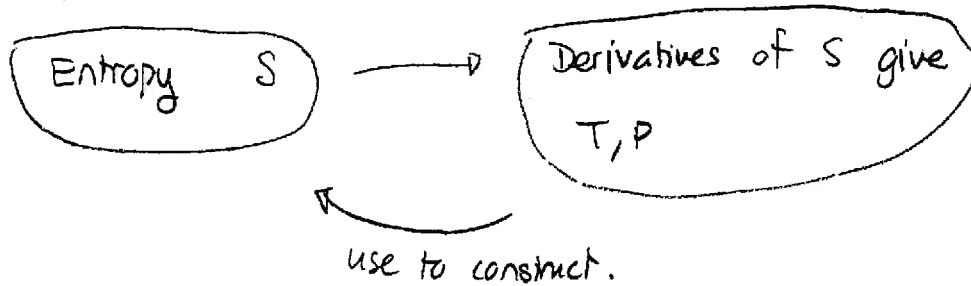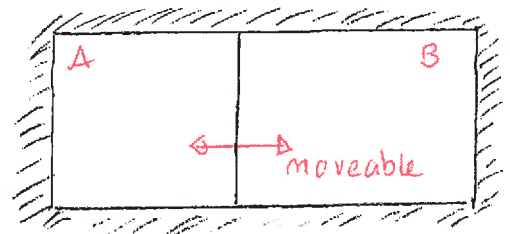S_f is a max

Pressure and temperature from entropy

Remarkably the second law gives mathematical rules that relate entropy to other thermodynamic variables. We will see.

Entropy S $\longrightarrow$ Derivatives of S give T, P

use to construct.

Consider two systems that are isolated from their surroundings but can interact with each other. We assume the following constraints

1) the number of particles in each subsystem is fixed

2) the total volume is fixed.

$$V = V_A + V_B$$

where $V_A =$ volume of A, $V_B =$ volume of B.

We also know, by the system's isolation that the total energy

$$E = E_A + E_B$$

is fixed. We now use the second law to derive a relationship between entropy and energy for the equilibrium state.

1 Temperature and Pressure from Entropy

Consider the scenario described in class. The state of each system can be described in terms of its energy, volume and particle number. Thus

$$S = S_A(E_A, V_A, N_A) + S_B(E_B, V_B, N_B).$$

a) First suppose that the volume of each subsystem is fixed. Then which of the variables E_A, V_A, N_A, E_B, V_B, and N_B are constant and which are not?

b) Are E_A and E_B independent? Provide a relationship between them.

c) Which of all the parameters in the expression for S actually vary in this situation? Use your answer and apply the strong version of the second law to determine a condition that S_A and S_B must satisfy for the system to be in equilibrium.

d) If energy is the only quantity that can be exchanged between the systems, then which macroscopic quantity should be the same for the two systems once they have reached equilibrium?

e) Now suppose that the volumes of the systems can vary. Repeat the analysis to determine a second condition that S_A and S_B must satisfy for the system to be in equilibrium. What macroscopic quantity should be the volumes have adjusted so that the two systems once they have reached equilibrium?

Answer: a) N_A, N_B fixed

V_A, V_B fixed

E_A, E_B can vary.

b) No. $E = E_A + E_B$ = constant

$E_B = E - E_A$ $\Rightarrow$ $E_B = E_B(E_A)$

c)   Just E_A. So for a maximum

$$\frac{\partial S}{\partial E_A} = 0$$

$\Rightarrow$ $\frac{\partial S_A}{\partial E_A} + \frac{\partial}{\partial E_A} S_B(E_B; V_B, N_B) = 0$.

But

$$\frac{\partial}{\partial E_A} S_B = \frac{\partial S_B}{\partial E_B} \frac{\partial E_B}{\partial E_A}$$

$$= \frac{\partial S_B}{\partial E_B} (-1)$$

So $\frac{\partial S_A}{\partial E_A} - \frac{\partial S_B}{\partial E_B} = 0$. $\Rightarrow$ In equilibrium $\boxed{\frac{\partial S_A}{\partial E_A} = \frac{\partial S_B}{\partial E_B}}$

d) The temperature must be the same. So

T_A must be related to $\frac{\partial S_A}{\partial E_A}$

T_B "   "   "   " $\frac{\partial S_B}{\partial E_B}$

e) By a similar reasoning

$$V_B = V - V_A$$

and

$$\frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = 0 \qquad \Rightarrow \qquad \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_B}\left(\frac{\partial V_B}{\partial V_A}\right) = 0$$

$$\Rightarrow \quad \frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B} = 0 \quad \Rightarrow \quad \boxed{\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}}$$

In equilibrium the two pressures must be related. So

$$P_A \rightsquigarrow \text{ related to } \frac{\partial S_A}{\partial V_A}$$

etc,...

We have seen that in equilibrium:

$$\frac{\partial S}{\partial E} \quad \rightsquigarrow \quad \text{has to do with temperature}$$

$$\frac{\partial S}{\partial V} \quad \rightsquigarrow \quad \text{''} \quad \text{''} \quad \text{''} \quad \text{''} \quad \text{pressure.}$$

We will need to find exact relationships between these and eventually check that they yield our usual notions of temperature and pressure.

2 Entropy changes and pressure and temperature

Consider a composite system as before and assume that each subsystem has fixed particle number. Thus

$$S = S_A(E_A, V_A, N_A) + S_B(E_B, V_B, N_B).$$

Suppose that the system is not in equilibrium and that $T_A > T_B$.

a) Assume that the system undergoes a quasistatic process. Determine an expression for dS in terms of dE_A, dE_B, dV_A, and dV_B.

b) Suppose that the volume of each subsystem is fixed and that the total energy is fixed. Determine an expression for dS in terms of dE_A.

c) Apply the second law of thermodynamics to find an inequality relating

$$\frac{\partial S_A}{\partial E_A} \quad \text{and} \quad \frac{\partial S_B}{\partial E_B}.$$

d) Which of the following is consistent with your result from the previous part

$$\frac{\partial S}{\partial E} = T \quad \text{or} \quad \frac{\partial S}{\partial E} = \frac{1}{T}?$$

Answer:

a) $dS = \left(\dfrac{\partial S_A}{\partial E_A}\right)_{V_A, N_A} dE_A + \left(\dfrac{\partial S_A}{\partial V_A}\right)_{E_A, N_A} dV_A$

$\quad + \left(\dfrac{\partial S_B}{\partial E_B}\right)_{V_B, N_B} dE_B + \left(\dfrac{\partial S_B}{\partial V_B}\right)_{E_B, N_B} dV_B$

b) $dV_A = 0$

$dV_B = 0$

Then $\qquad E = E_A + E_B$ is constant

$\qquad \Rightarrow dE = 0 \quad \Rightarrow dE_A + dE_B = 0 \quad \Rightarrow dE_B = -dE_A$

$\Rightarrow dS = \left[\left(\dfrac{\partial S_A}{\partial E_A}\right)_{V_A, N_A} - \left(\dfrac{\partial S_B}{\partial E_B}\right)_{V_B, N_B} \right] dE_A$

c) We need $dS \geqslant 0$

$\Rightarrow \left[\left(\dfrac{\partial S_A}{\partial E_A}\right)_{V_A, N_A} - \left(\dfrac{\partial S_B}{\partial E_B}\right)_{V_B, N_B} \right] dE_A \geqslant 0$

We usually observe that the temperature of A decreases if $T_{A_i} > T_{B_i}$
So requiring E_A to increase with T_A means $dE_A < 0$. Thus

$\left(\dfrac{\partial S_B}{\partial E_B}\right)_{V_B, N_B} \geqslant \left(\dfrac{\partial S_A}{\partial E_A}\right)_{V_A, N_A}$

d) If the first then $\quad T_B > T_A \quad$ not possible

   If the second " $\quad T_B < T_A \quad$ possible.

We therefore define

The thermodynamic temperature of a system is

$$T_{th} = \cfrac{1}{\left(\dfrac{\partial S}{\partial E}\right)_{V,N}}$$

We will eventually show that for certain ideal gas processes the conventional temperature satisfies $T = T_{th}$. Thus we get

$$T = \cfrac{1}{\left(\dfrac{\partial S}{\partial E}\right)_{V,N}}$$

So we now have a mathematically precise scheme for defining temperature:

Express $E = E(P, V, N)$

$S = S(P, V, N)$

Rearrange to get

$$P = P(E, V, N)$$

and

$$S = S(E, V, N)$$

Temperature is

$$T = \cfrac{1}{\left(\dfrac{\partial S}{\partial E}\right)_{V,N}}$$