

# Fundamentals of Thermodynamics

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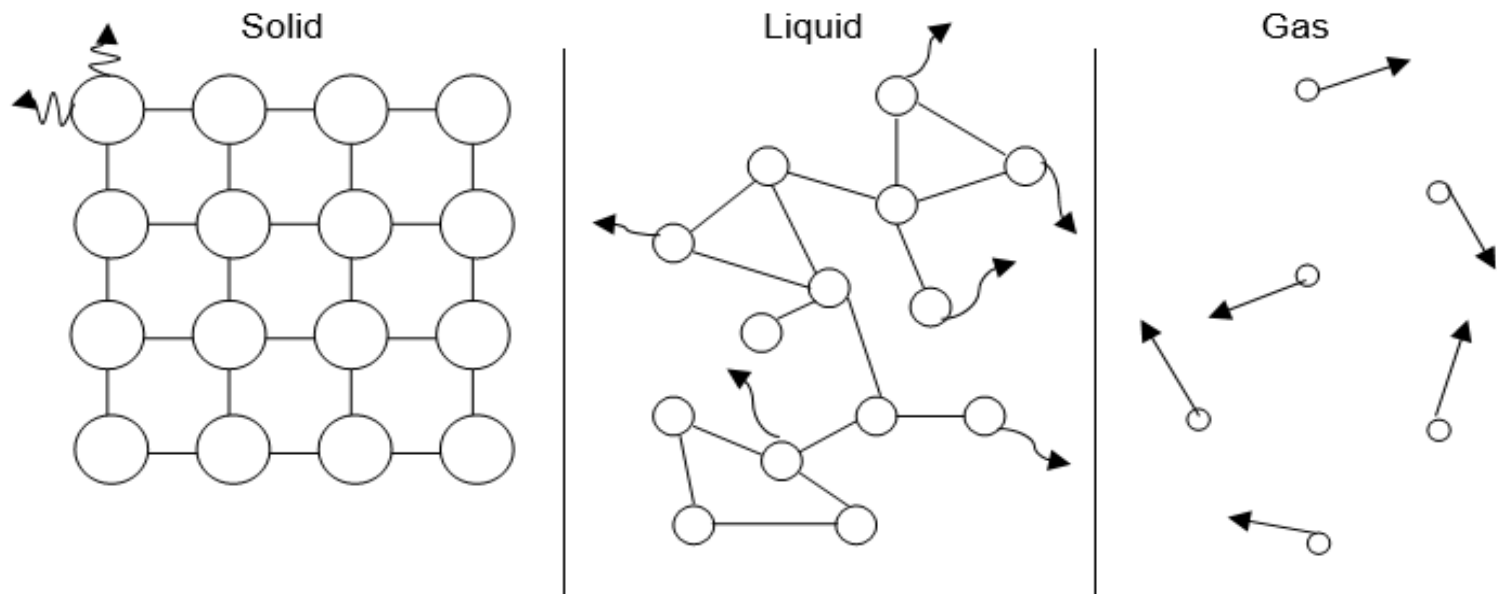


1. Substances and ideal gas
2. First Law of Thermodynamics
3. Steady Flow Energy Equation
4. Second Law of Thermodynamics
5. Entropy



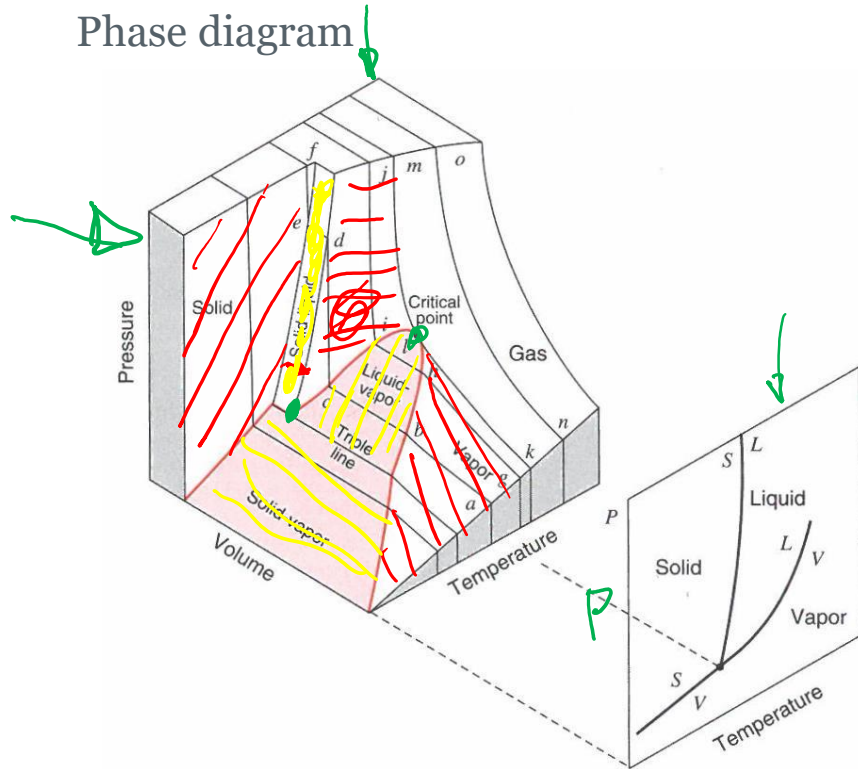
## Phases

A **phase** is defined as a quantity of matter that is homogeneous throughout.

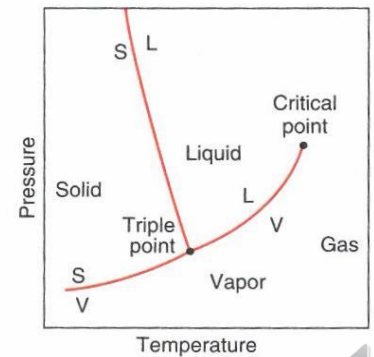
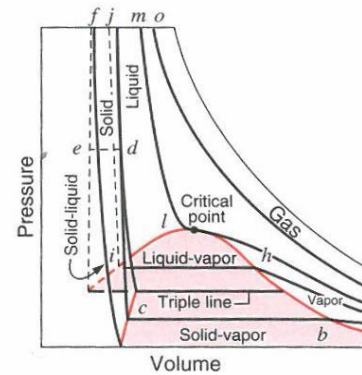
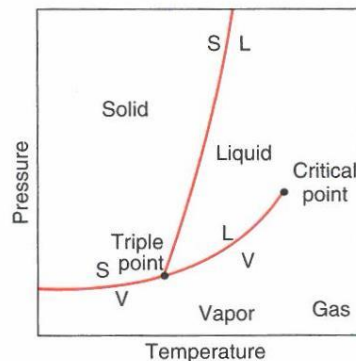
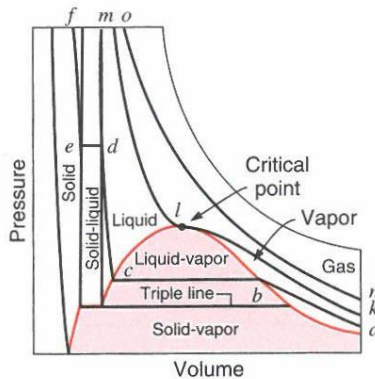
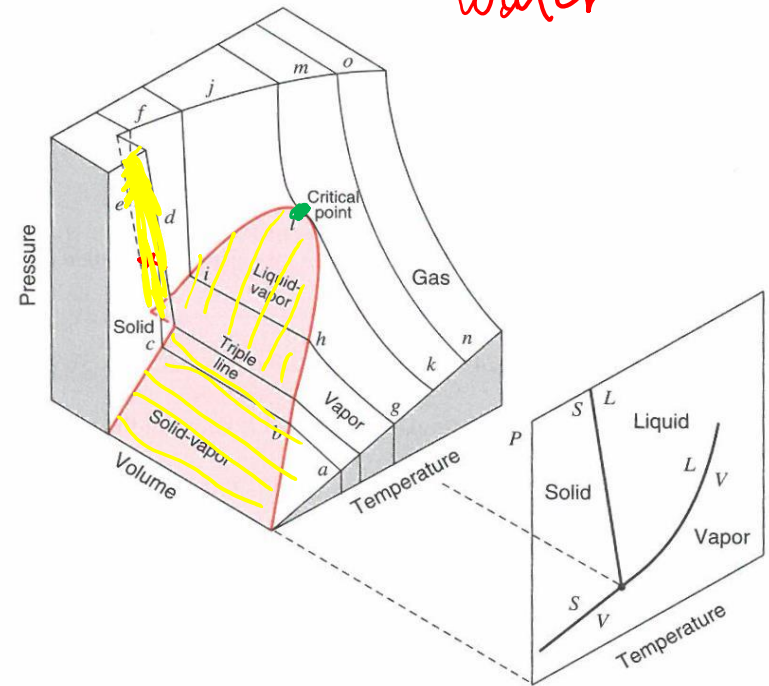


# Substances

## Phase diagram



water



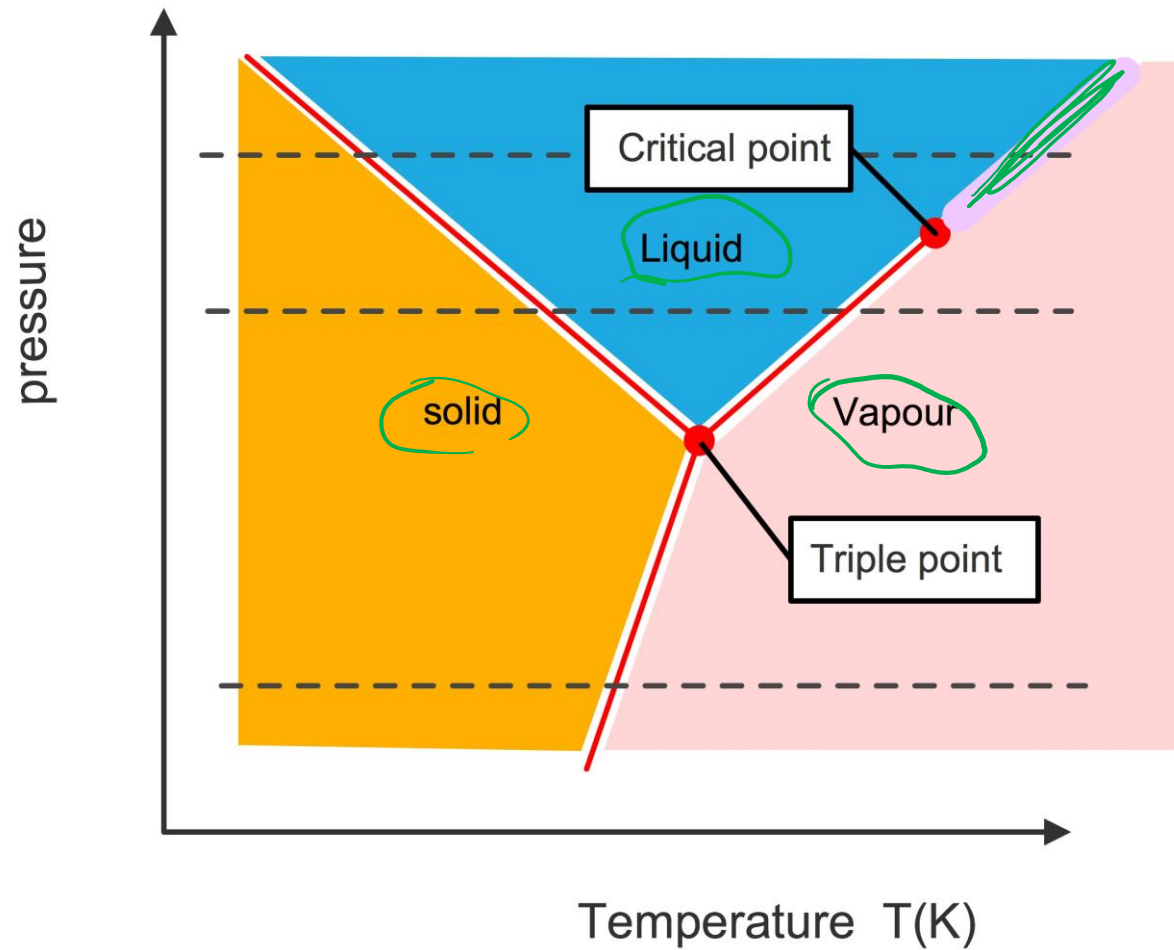
Phase diagram of a substance that contracts on freezing

Friday, 20 March 2020

Phase diagram of a substance that expands on freezing



## Phase diagram

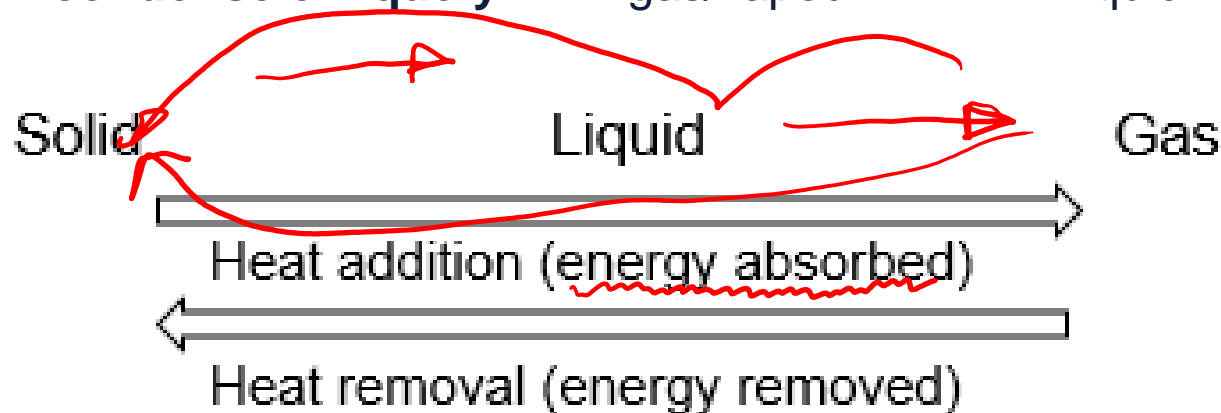


p-T diagram

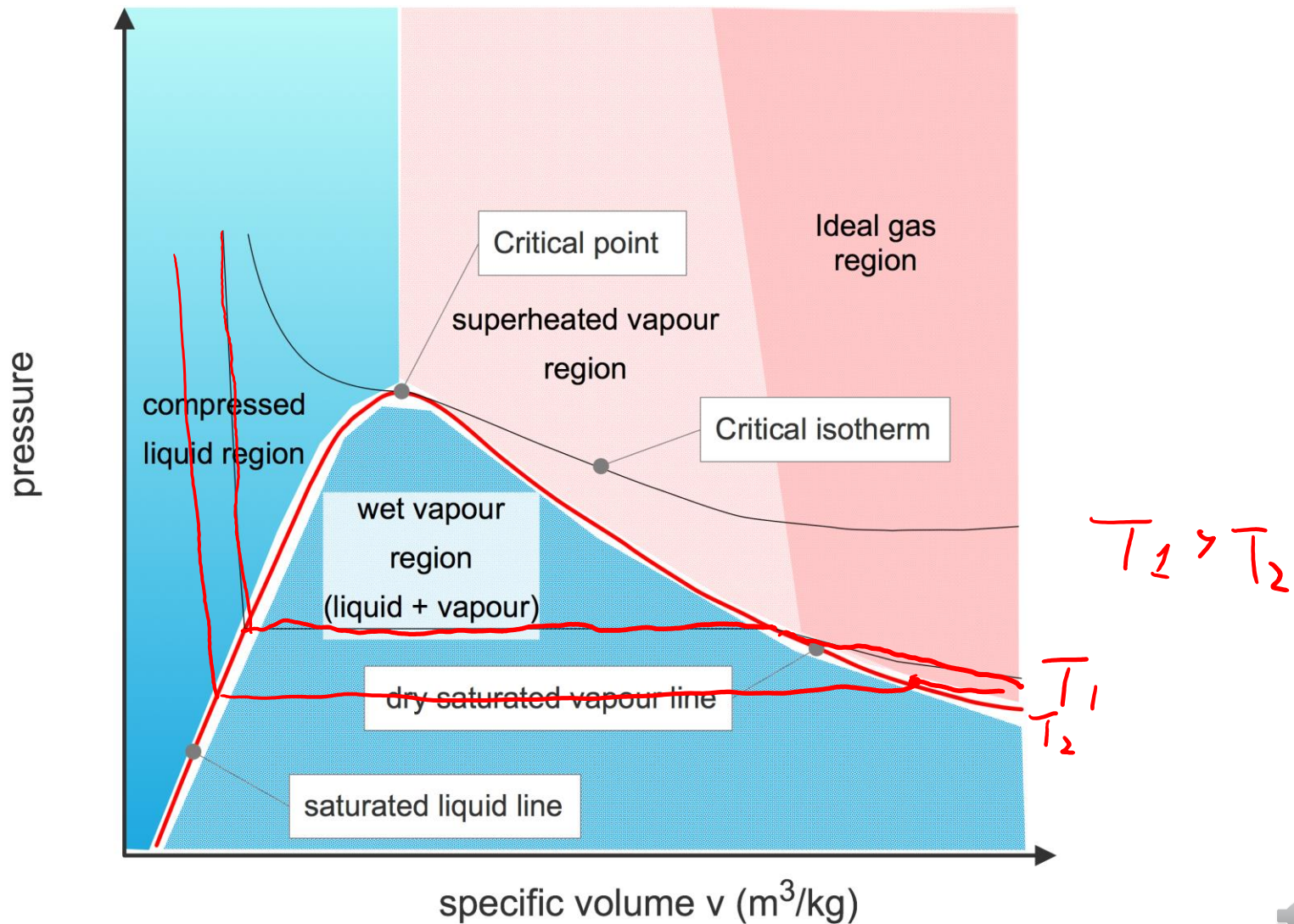
## Phase change

During phase change, substance exists simultaneously in two phase at the same temperature. In this process the **temperature remains constant at constant pressure** until the process finishes.

Terminology: <b>freeze</b> or <b>solidify</b> :	gas/vapour or liquid	→ solid
<b>melt</b> or <b>fuse</b> :	solid	→ liquid
<b>sublimate</b> :	solid	→ gas/vapour
<b>boil</b> or <b>evaporate</b> :	liquid	→ gas/vapour
<b>condense</b> or <b>liquefy</b> :	gas/vapour	→ liquid



## Phase diagram and terminology



## Phase change

The energy transferred at constant temperature during change of phase is (specific) **latent heat**

$$Q = m\lambda \quad \text{where } \lambda \text{ (J/kg) is specific latent heat}$$

The energy transferred in single phase resulting in temperature change is **sensible heat**.

$$Q = mc\Delta T \quad \text{where } c \text{ (J/kg K) is specific heat capacity}$$

Latent heat  $\lambda$  has two components: changing molecular potential energy and specific work done by/against surroundings at constant pressure  $p\Delta V$  due to change in volume when phase changes.



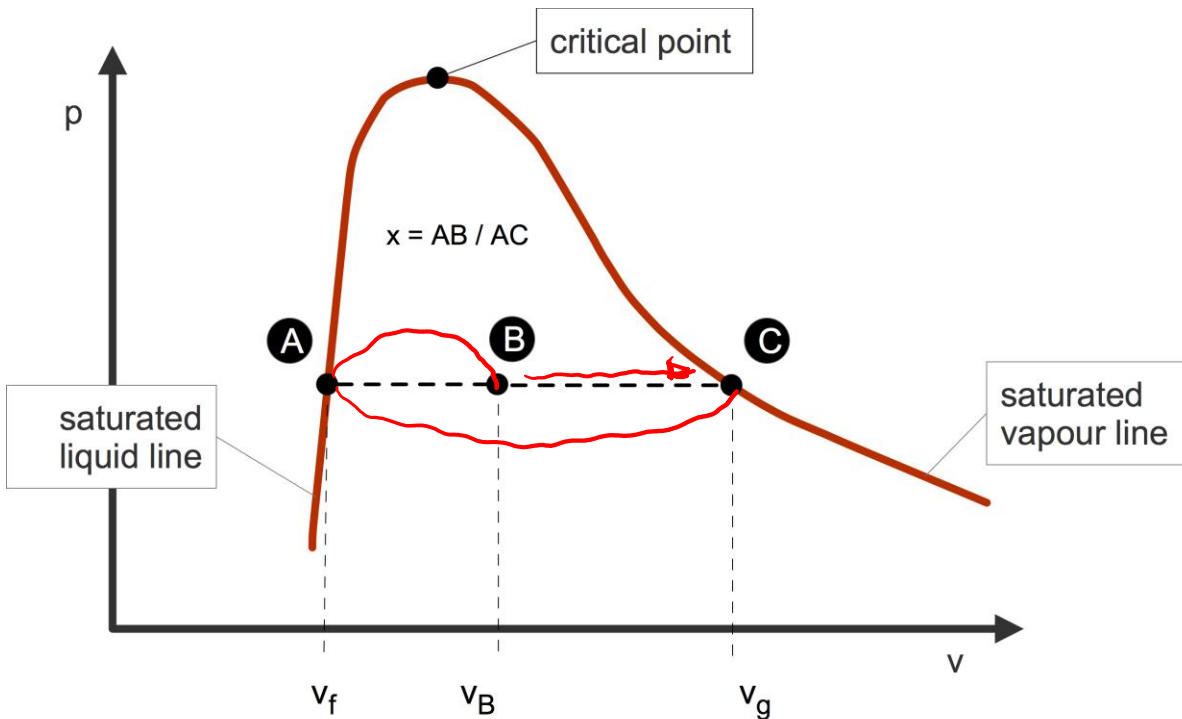
## Phase change

rem

Dry fraction (quality) and property table to be introduced in next semester  
Thermodynamics

$x$  = Quality or Dryness fraction

Relates to horizontal distances  
on  
p-v or T-v diagrams



Dryness fraction ( $x$ ) =  $\frac{\text{mass of pure vapour in mixture}}{\text{mass of liquid and vapour}}$

# Steam table

## How to read a steam table

Saturated Water and Steam

$T$ [°C]	$p_s$ [bar]	$v_g$ [m³/kg]	$h_f$	$h_{fg}$	$h_g$	$s_f$	$s_{fg}$	$s_g$
			[kJ/kg]			[kJ/kg K]		
0.01	0.006112	206.1	0*	2500.8	2500.8	0†	9.155	9.155
1	0.006566	192.6	4.2	2498.3	2502.5	0.015	9.113	9.128
2	0.007054	179.9	8.4	2495.9	2504.3	0.031	9.071	9.102
3	0.007575	168.2	12.6	2493.6	2506.2	0.046	9.030	9.076
4	0.008129	157.3	16.8	2491.3	2508.1	0.061	8.989	9.050
5	0.008719	147.1	21.0	2488.9	2509.9	0.076	8.948	9.024
6	0.009346	137.8	25.2	2486.6	2511.8	0.091	8.908	8.999
7	0.01001	129.1	29.4	2484.3	2513.7	0.106	8.868	8.974
8	0.01072	121.0	33.6	2481.9	2515.5	0.121	8.828	8.949
9	0.01147	113.4	37.8	2479.6	2517.4	0.136	8.788	8.924
10	0.01227	106.4	42.0	2477.2	2519.2	0.151	8.749	8.900
11	0.01312	99.90	46.2	2474.9	2521.1	0.166	8.710	8.876
12	0.01401	93.83	50.4	2472.5	2522.9	0.180	8.671	8.851
13	0.01497	88.17	54.6	2470.2	2524.8	0.195	8.633	8.828
14	0.01597	82.89	58.8	2467.8	2526.6	0.210	8.594	8.804
15	0.01704	77.97	62.9	2465.5	2528.4	0.224	8.556	8.780
16	0.01817	73.38	67.1	2463.1	2530.2	0.239	8.518	8.757
17	0.01936	69.09	71.3	2460.8	2532.1	0.253	8.481	8.734
18	0.02063	65.08	75.5	2458.4	2533.9	0.268	8.444	8.712
19	0.02196	61.34	79.7	2456.0	2535.7	0.282	8.407	8.689
20	0.02337	57.84	83.9	2453.7	2537.6	0.296	8.370	8.666
21	0.02486	54.56	88.0	2451.4	2539.4	0.310	8.334	8.644
22	0.02642	51.49	92.2	2449.0	2541.2	0.325	8.297	8.622
23	0.02808	48.62	96.4	2446.6	2543.0	0.339	8.261	8.600
24	0.02982	45.92	100.6	2444.2	2544.8	0.353	8.226	8.579
25	0.03166	43.40	104.8	2441.8	2546.6	0.367	8.190	8.557
26	0.03360	41.03	108.9	2439.5	2548.4	0.381	8.155	8.536
27	0.03564	38.81	113.1	2437.2	2550.3	0.395	8.120	8.515
28	0.03778	36.73	117.3	2434.8	2552.1	0.409	8.085	8.494
29	0.04004	34.77	121.5	2432.4	2553.9	0.423	8.050	8.473
30	0.04242	32.93	125.7	2430.0	2555.7	0.436	8.016	8.452
32	0.04754	29.57	134.0	2425.3	2559.3	0.464	7.948	8.417
34	0.05318	26.60	142.4	2420.5	2562.9	0.491	7.881	8.372
36	0.05940	23.97	150.7	2415.8	2566.5	0.518	7.814	8.332
38	0.06624	21.63	159.1	2411.0	2570.1	0.545	7.749	8.294
40	0.07375	19.55	167.5	2406.2	2573.7	0.572	7.684	8.256
42	0.08198	17.69	175.8	2401.4	2577.2	0.599	7.620	8.219
44	0.09100	16.03	184.2	2396.6	2580.8	0.625	7.557	8.182
46	0.1009	14.56	192.5	2391.8	2584.3	0.651	7.494	8.145
48	0.1116	13.23	200.9	2387.0	2587.9	0.678	7.433	8.111
50	0.1233	12.04	209.3	2382.1	2591.4	0.704	7.371	8.075
55	0.1574	9.578	230.2	2370.1	2600.3	0.768	7.223	7.991
60	0.1992	7.678	251.1	2357.9	2609.0	0.831	7.078	7.909
65	0.2501	6.201	272.0	2345.7	2617.7	0.893	6.937	7.830
70	0.3116	5.045	293.0	2333.3	2626.3	0.955	6.800	7.755
75	0.3855	4.133	313.9	2320.8	2634.7	1.015	6.666	7.681
80	0.4736	3.408	334.9	2308.3	2643.2	1.075	6.536	7.611
85	0.5780	2.828	355.9	2295.6	2651.5	1.134	6.410	7.544
90	0.7011	2.361	376.9	2282.8	2659.7	1.192	6.286	7.478
95	0.8453	1.982	398.0	2269.8	2667.8	1.250	6.166	7.416
100	1.01325	1.673	419.1	2256.7	2675.8	1.307	6.048	7.355

\*  $h_f$  and  $s_f$  are chosen to be zero for saturated liquid at the triple point.

Note: values of  $v_f$  can be found on p. 10.

Saturated Water and Steam

$p$ [bar]	$T_s$ [°C]	$v_g$ [m³/kg]	$u_f$	$u_{fg}$	$h_f$	$h_{fg}$	$h_g$	$s_f$	$s_{fg}$	$s_g$
			[kJ/kg]		[kJ/kg]			[kJ/kg K]		
0.006112	0.01	206.1	0†	2375	0*	2501	2501	0†	9.155	9.155
0.010	7.0	129.2	29	2385	29	2485	2514	0.106	8.868	8.974
0.015	13.0	87.98	55	2393	55	2470	2525	0.196	8.631	8.827
0.020	17.5	67.01	73	2399	73	2460	2533	0.261	8.462	8.723
0.025	21.1	54.26	88	2403	88	2451	2539	0.312	8.330	8.642
0.030	24.1	45.67	101	2408	101	2444	2545	0.354	8.222	8.576
0.035	26.7	39.48	112	2412	112	2438	2550	0.391	8.130	8.521
0.040	29.0	34.80	121	2415	121	2433	2554	0.422	8.051	8.473
0.045	31.0	31.14	130	2418	130	2428	2558	0.451	7.980	8.431
0.050	32.9	28.20	138	2420	138	2423	2561	0.476	7.918	8.394
0.055	34.6	25.77	145	2422	145	2419	2564	0.500	7.860	8.360
0.060	36.2	23.74	152	2425	152	2415	2567	0.521	7.808	8.329
0.065	37.7	22.02	158	2427	158	2412	2570	0.541	7.760	8.301
0.070	39.0	20.53	163	2428	163	2409	2572	0.559	7.715	8.274
0.075	40.3	19.24	169	2430	169	2405	2574	0.576	7.674	8.250
0.080	41.5	18.10	174	2432	174	2402	2576	0.593	7.634	8.227
0.085	42.7	17.10	179	2434	179	2400	2579	0.608	7.598	8.206
0.090	43.8	16.20	183	2435	183	2397	2580	0.622	7.564	8.186
0.095	44.8	15.40	188	2436	188	2394	2582	0.636	7.531	8.167
0.100	45.8	14.67	192	2437	192	2392	2584	0.649	7.500	8.149
0.12	49.4	12.36	207	2442	207	2383	2590	0.696	7.389	8.085
0.14	52.6	10.69	220	2446	220	2376	2596	0.737	7.294	8.031
0.16	55.3	9.432	232	2450	232	2369	2601	0.772	7.213	7.985
0.18	57.8	8.444	242	2453	242	2363	2605	0.804	7.140	7.944
0.20	60.1	7.648	251	2456	251	2358	2609	0.832	7.075	7.907
0.22	62.2	6.994	260	2459	260	2353	2613	0.858	7.016	7.874
0.24	64.1	6.445	268	2461	268	2348	2616	0.882	6.962	7.844
0.26	65.9	5.979	276	2464	276	2343	2619	0.904	6.913	7.817
0.28	67.5	5.578	283	2466	283	2339	2622	0.925	6.866	7.791
0.30	69.1	5.228	289	2468	289	2336	2625	0.944	6.823	7.767
0.32	70.6	4.921	295	2470	295	2332	2627	0.962	6.783	7.745
0.34	72.0	4.649	302	2472	302	2328	2630	0.980	6.745	7.725
0.36	73.4	4.407	307	2473	307	2325	2632	0.996	6.709	7.705
0.38	74.7	4.189	312	2475	312	2322	2634	1.011	6.675	7.686
0.40	75.9	3.992	318	2476	318	2318	2636	1.026	6.643	7.669
0.42	77.1	3.814	323	2478	323	2315	2638	1.040	6.617	7.652
0.44	78.2	3.651	327	2479	327	2313	2640	1.054	6.582	7.636
0.46	79.3	3.502	332	2481	332	2310	2642	1.067	6.554	7.621
0.48	80.3	3.366	336	2482	336	2308	2644	1.079	6.528	7.607
0.50	81.3	3.239	340	2483	340	2305	2645	1.091	6.502	7.593
0.55	83.7	2.964	351	2486	351	2298	2649	1.119	6.442	7.561
0.60	86.0	2.731	360	2489	360	2293	2653	1.145	6.386	7.531
0.65	88.0	2.535	369	2492	369	2288	2657	1.169	6.335	7.504
0.70	90.0	2.364	377	2494	377	2283	2660	1.192	6.286	7.478
0.75	91.8	2.217	384	2496	384	2278	2662	1.213	6.243	7.456
0.80	93.5	2.087	392	2498	392	2273	2665	1.233	6.201	7.434
0.85	95.2	1.972	399	2500	399	2269	2668	1.252	6.162	7.414
0.90	96.7	1.869	405	2502	405	2266	2671	1.270	6.124	7.394
0.95	98.2	1.777	411	2504	411	2262	2673	1.287	6.089	7.376
1.00	99.6	1.694	417	2506	417	2258	2675	1.303	6.056	7.359

$$\begin{aligned}
 \frac{h_f}{[\text{kJ/kg}]} &= \frac{p v_f}{[\text{kJ/kg}]} = \frac{p}{[\text{bar}]} \times \frac{10^5 [\text{N}]}{[\text{m}^2]} \times \frac{v_f}{[\text{m}^3/\text{kg}]} \times \frac{[\text{kg}]}{[\text{kg}]} \times \frac{[\text{kJ}]}{10^3 [\text{N m}]} \times \frac{1}{[\text{kJ/kg}]} \\
 &= \frac{p}{[\text{bar}]} \times \frac{v_f}{[\text{m}^3/\text{kg}]} \times 10^2 = 0.006112 \times 0.0010002 \times 10^2 = 0.0006112
 \end{aligned}$$

# Steam table

Linear interpolation

Example:

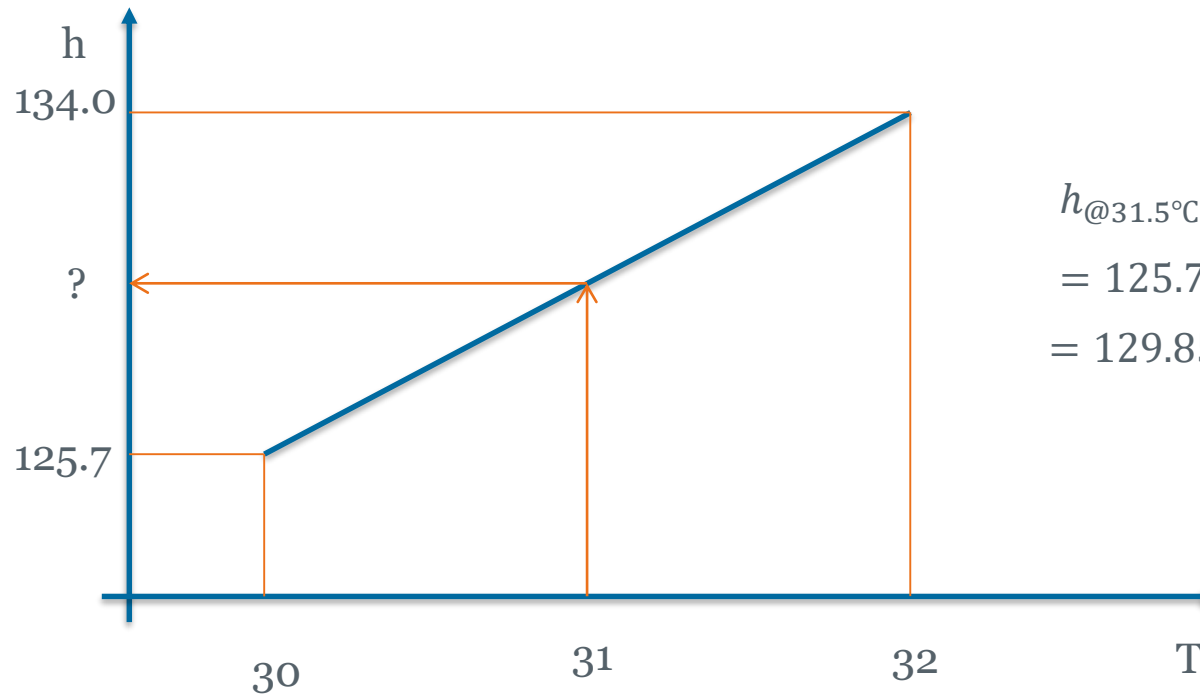
Determine the specific enthalpy of water at 31°C.

T	p	$v_g$	$h_f$	$h_{fg}$	$h_g$
°C	bar	m <sup>3</sup> /kg	kJ/kg	kJ/kg	kJ/kg
0.01	0.006112	206.1	0	2500.8	2500.8
30	0.04242	32.93	125.7	2430.0	2555.7
32	0.04754	29.57	134.0	2425.3	2559.3
100	1.01325	1.673	419.1	2256.7	2675.8

# Steam table

## Linear interpolation

T	p	$v_g$	$h_f$	$h_{fg}$	$h_g$
°C	bar	m <sup>3</sup> /kg	kJ/kg	kJ/kg	kJ/kg
0.01	0.006112	206.1	0	2500.8	2500.8
30	0.04242	32.93	125.7	2430.0	2555.7
32	0.04754	29.57	134.0	2425.3	2559.3
100	1.01325	1.673	419.1	2256.7	2675.8



$$\begin{aligned} h_{@31.5^{\circ}\text{C}} &= 125.7 + \frac{31 - 30}{32 - 30} (134 - 125.7) \\ &= 129.85 \text{ kJ/kg} \end{aligned}$$

# Steam table

## General rules of using property tables

Step 1. Decide the phase of the substance (single gas, single liquid, or two-phase);

Step 2. Use the appropriate tables (substance and phase);

Step 3. Work out the properties. Interpolate if needed.



# Ideal gas

## Ideal gas equations

### Boyle's Law

$pV = \text{constant}$ , at constant temperature

### Charle's (or Gay-Lussac's) Law

$V/T = \text{constant}$ , at constant pressure

Combine:

$$pV = mRT$$

*specific gas constant*  
*Temperature (K)*

where  $R$  (J/kg K) is a **constant for a specific gas**

### Avogadro's Law

$$pV = nR_0T$$

*mass* → *mole number* → *universal gas constant*

where  $n$  is the mole number and  $R_0$  is the  
**universal constant for all gases**  $R_0 = 8314$  (J/kmol K)

$$M \equiv m/n \quad \text{therefore } R = R_0/M$$

# Ideal gas

## Ideal gas approximations

- All molecules are identical
- Sufficiently large numbers of molecules for statistics to be significant
- Molecular motion is continuous and random
- Law of Newtonian physics apply at molecular scale
- \*Attractive forces between molecules are negligible
- \*Any collisions between molecules and with walls of container are perfectly elastic
- \*Molecules occupy negligible volume themselves

last three items imply that the ideal gas approximations are only valid when in the region of modest temperature and pressure of **gas phase**.



# Ideal gas

## Mixture of gases

$$m_{tot} = m_1 + m_2 + \dots + m_N = \sum m_i$$

$$n_{tot} = n_1 + n_2 + \dots + n_N = \sum n_i$$

Mass fraction of component i:

$$x_{mi} = \frac{m_i}{m_{tot}}$$

Mole fraction of component i:

$$x_{ni} = \frac{n_i}{n_{tot}}$$

To calculate mass fraction from mole fraction

$$x_{mi} = \frac{n_i M_i}{m_{tot}} = \frac{n_i M_i}{\sum n_j M_j} = \frac{n_i M_i / n_{tot}}{\sum n_j M_j / n_{tot}} = \frac{x_{ni} M_i}{\sum x_{nj} M_j}$$

To calculate mole fraction from mass fraction

$$x_{ni} = \frac{m_i / M_i}{n_{tot}} = \frac{m_i / M_i}{\sum m_j / M_j} = \frac{m_i / (M_i m_{tot})}{\sum m_j / (M_j m_{tot})} = \frac{x_{mi} / M_i}{\sum x_{mj} / M_j}$$

# Ideal gas

## Mixture of ideal gases

The molar mass of the mixture becomes:

$$M_{mix} = \frac{m_{tot}}{n_{tot}} = \frac{\sum m_i}{n_{tot}} = \frac{\sum n_i M_i}{n_{tot}} = \sum x_{ni} M_i$$

**Gibb's Law** for extensive properties of any mixture (not just ideal gas)

$$\Phi_{tot} = \sum \Phi_i$$

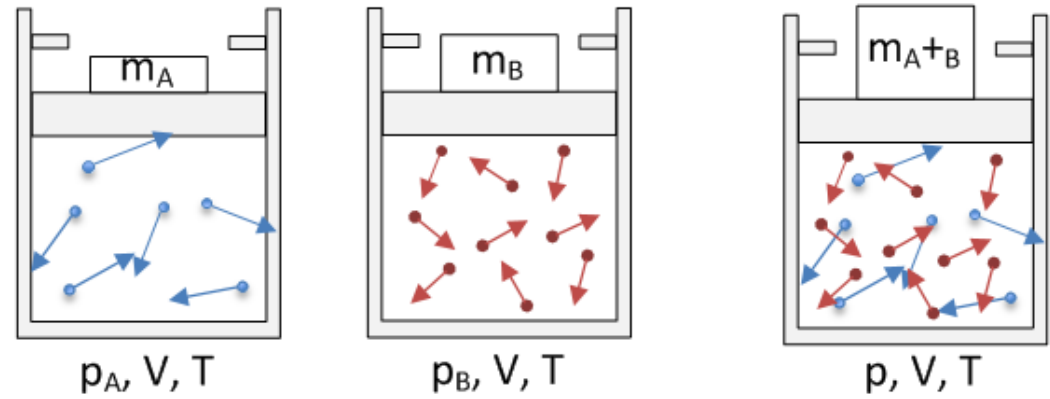
$$\text{e.g. } \underline{U_{tot}} = \sum \underline{U_i} \quad \text{or} \quad H_{tot} = \sum H_i$$

# Ideal gas

## Dalton model

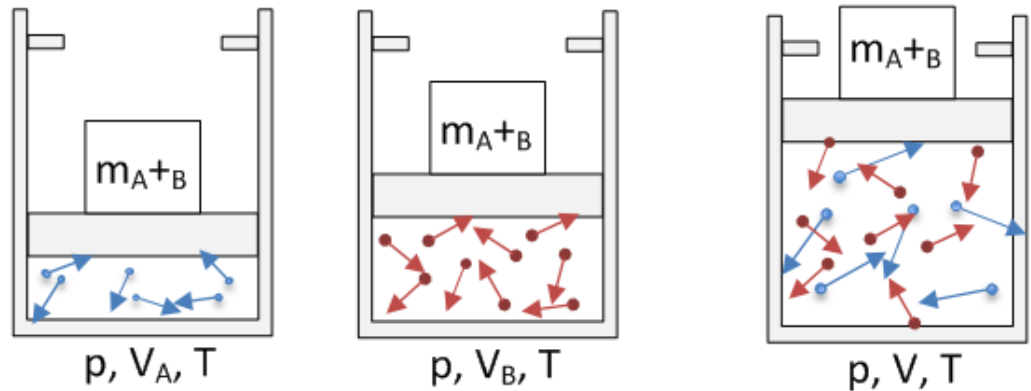
### Partial pressure

$$p = p_A + p_B$$



### partial volume

$$V = V_A + V_B$$



$$p_i V_{tot} = n_i R_0 T \quad \text{or} \quad p_{tot} V_i = n_i R_0 T$$

$$p_i = \frac{n_i R_0 T}{V_{tot}} = \frac{n_i}{n_{tot}} p_{tot} \quad \text{or} \quad V_i = \frac{n_i R_0 T}{p_{tot}} = \frac{n_i}{n_{tot}} V_{tot}$$

$$x_{pi} \equiv x_{ni} \equiv x_{vi}$$



# The First Law of thermodynamics

## The First Law

**When a system is taken through a cycle, the cyclic integral of the heat is proportional to the cyclic integral of the work.**

$$\sum Q - \sum W = 0$$

In integral form

$$\oint dQ - \oint dW = 0$$

Note: in some references you may find the first law is written in the form of  $\oint \delta Q + \oint \delta W = 0$ . This sign conversion is totally arbitrary and in this case, the work is defined as  $dW = -pdV$ .

# The First Law of thermodynamics

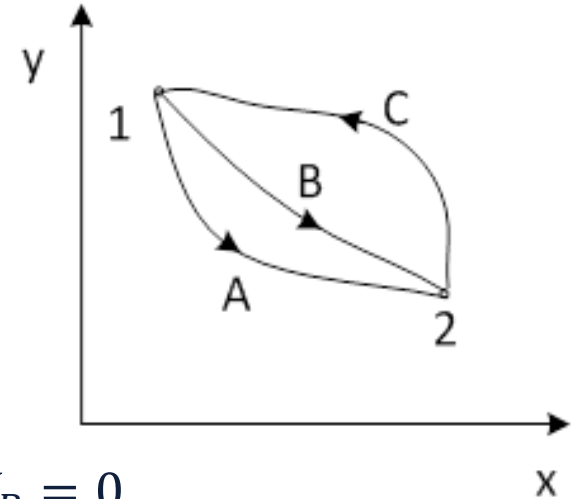
System energy

Corollary of the First Law:

If we consider two cycles AC and BC

$$\text{AC: } \int_1^2 dQ_A + \int_2^1 dQ_C - \int_1^2 dW_A - \int_2^1 dW_C = 0$$

$$\text{BC: } \int_1^2 dQ_B + \int_2^1 dQ_C - \int_1^2 dW_B - \int_2^1 dW_C = 0$$



Subtracting the second from the first

$$\int_1^2 dQ_A - \int_1^2 dQ_B - \int_1^2 dW_A + \int_1^2 dW_B = 0$$

Rearrange:

$$\int_1^2 (dQ - dW)_A = \int_1^2 (dQ - dW)_B$$

Implies: quantity (Q-W) depends only on the initial and final states

We define Energy:  $E = Q - W$

Or  $dE = \delta Q - \delta W$

# The First Law of thermodynamics

Energy forms conservation of energy

Potential Energy:  $PE = mg(z - z_0)$

Kinetic Energy:  $KE = mc^2$   
or rotating body:  $KE = I \omega^2$

Internal Energy:  $U = f(T)$   
 $E = U + \left(\frac{1}{2}mc^2\right) + (mgZ) + \text{etc. (electrical)}$

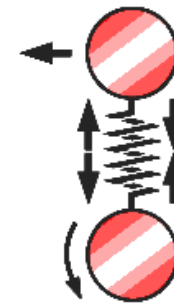
Or  $dE = dU + d(KE) + d(PE) = dU +$

First Law:

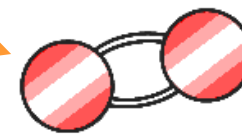
$$Q - W = E_2 - E_1 = (U_2 + \frac{1}{2}mc^2 + m_i$$

Or in specific form:

$$q - w = \Delta(u + \frac{1}{2}c^2 + gz)$$



**SENSIBLE  
AND LATENT  
ENERGY**



**CHEMICAL  
ENERGY**

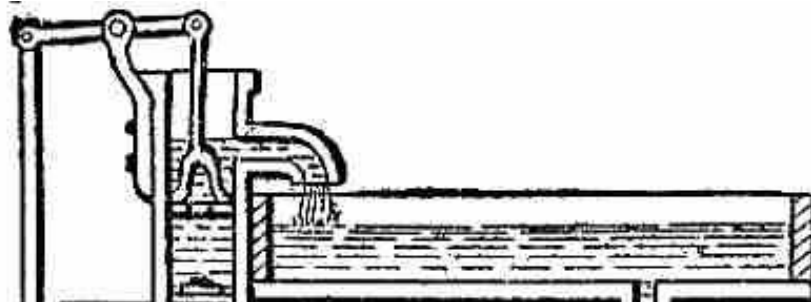
.....)



**NUCLEAR  
ENERGY**

# The First Law of thermodynamics

Conservation of energy and first type perpetual machine



**Conservation of energy:** the net change of the energy of the control mass is always equal to the net transfer of energy across the boundary as heat and work.



Energy is neither created nor destroyed, it only changes form.



# The First Law of thermodynamics

Non-flow energy equation

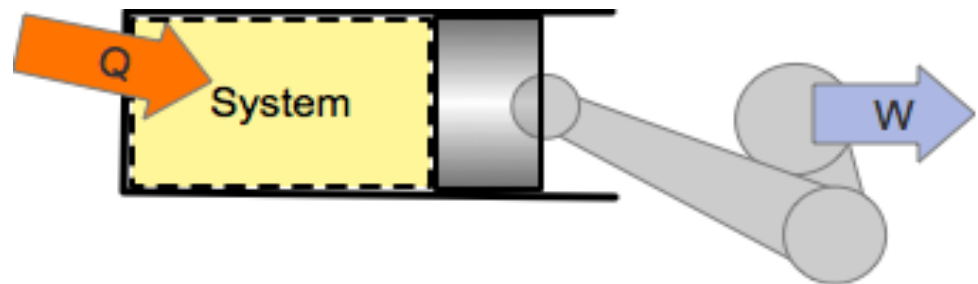
General energy form

$$q - w = \Delta(u + \frac{1}{2}c^2 + gz)$$

For NON-FLOW process this is approximated by

$$q - w = u_2 - u_1$$

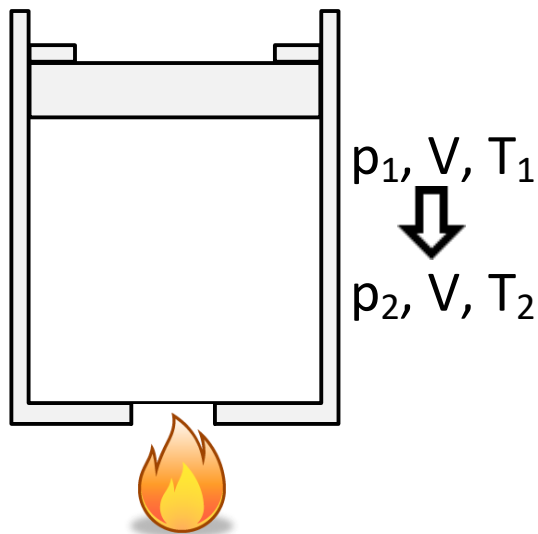
P.E. and K.E are neglected as they are small in comparison with the change in internal energy.



# The First Law of thermodynamics

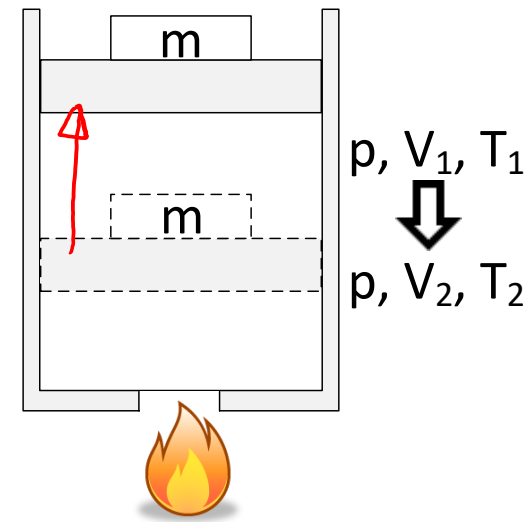
## Specific heat capacities

**Specific heat (capacity)** is the energy supplied to raise the unit mass of the substance one unit of temperature



$$c_V = \frac{1}{m} \left[ \frac{\Delta Q}{\Delta T} \right]_V = \left[ \frac{\Delta q}{\Delta T} \right]_V$$

Specific heat capacity at constant volume



$$c_p = \frac{1}{m} \left[ \frac{\Delta Q}{\Delta T} \right]_p = \left[ \frac{\Delta q}{\Delta T} \right]_p$$

Specific heat capacity at constant pressure

$$C_p > C_v$$

# The First Law of thermodynamics

Constant volume specific heat

From the First Law

$$du = dq - dw = dq - p dv$$

As constant volume:

$$dv = 0$$

Therefore:

$$c_V = \left[ \frac{\Delta q}{\Delta T} \right]_V = \left[ \frac{\partial u}{\partial T} \right]_V$$

Because

$$u = f(T, v)$$

For general change:

$$du = \left[ \frac{\partial u}{\partial T} \right]_V dT + \left[ \frac{\partial u}{\partial V} \right]_T dV = c_V dT + \left[ \frac{\partial u}{\partial V} \right]_T dV$$

By Gay-Lussac's experiment

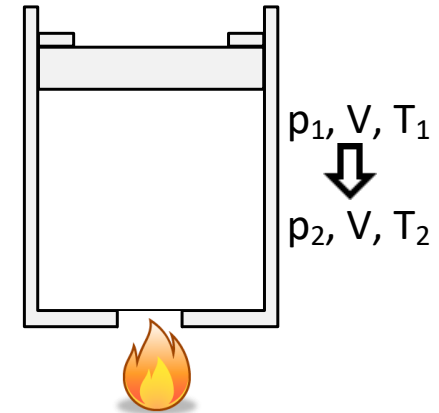
$$\left[ \frac{\partial u}{\partial V} \right]_T = 0$$

Therefore

$$du = \left[ \frac{\partial u}{\partial T} \right]_V dT = c_V dT$$

Or for constant  $c_V$

$$u_2 - u_1 = c_V (T_2 - T_1)$$



$$c_V = \frac{1}{m} \left[ \frac{\Delta Q}{\Delta T} \right]_V = \left[ \frac{\Delta q}{\Delta T} \right]_V$$

$$c_V = \frac{du}{dT}$$

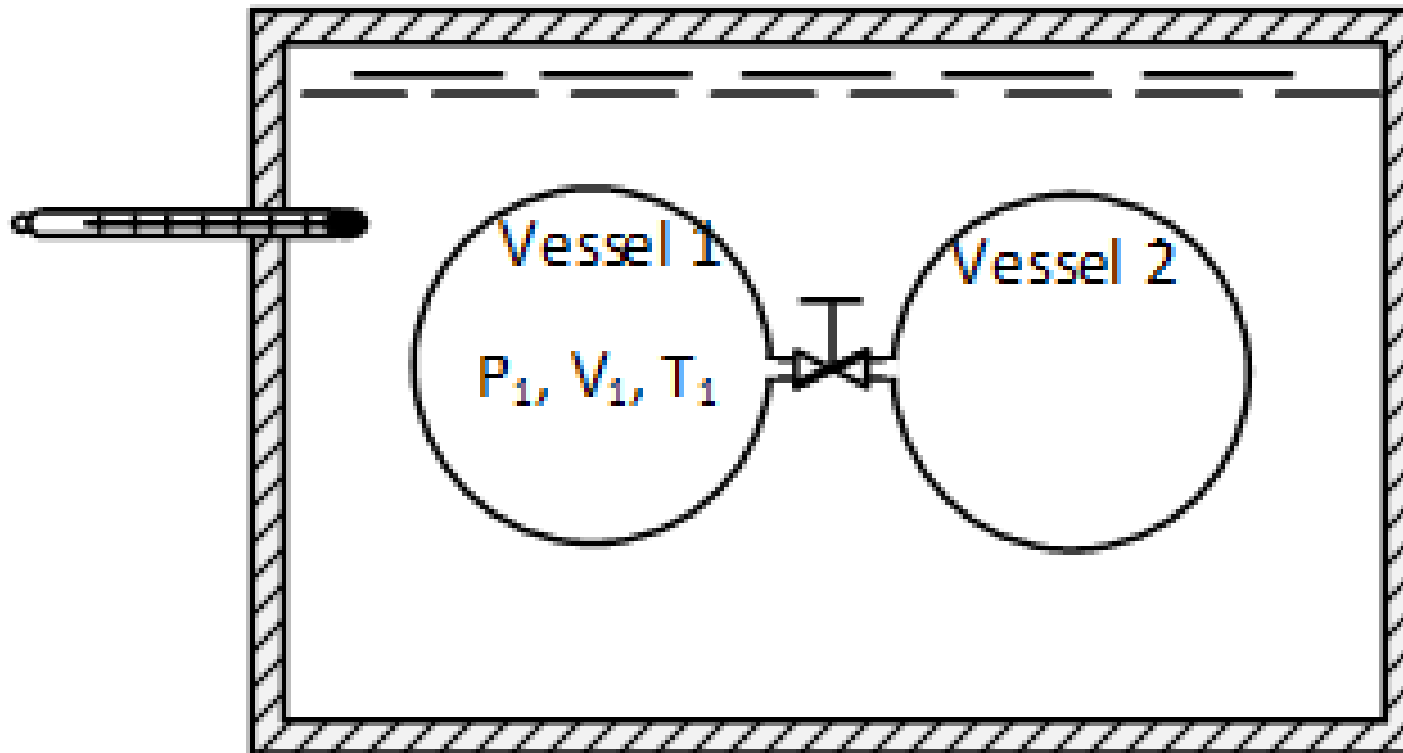
(ideal gas)

**Only for ideal gases!**

# The First Law of Thermodynamics

Gay-Lussac's (Joule's) experiment

$U \leftrightarrow T$



$$\left[ \frac{\partial u}{\partial V} \right]_T = 0$$

# The First Law of Thermodynamics

## Enthalpy and Constant pressure specific heat

We define **Enthalpy**,  $h$  or  $H$  by

$$\boxed{h = u + p \cdot v} \quad \text{or} \quad \boxed{H = U + p \cdot V}$$

Hence  $dh = du + p \cdot dv + v \cdot dp$

Substitute to the First Law:  $dq = dh - v \cdot dp$

Constant pressure specific heat:  $c_p = \frac{1}{m} \left[ \frac{\Delta Q}{\Delta T} \right]_p = \left[ \frac{\Delta q}{\Delta T} \right]_p$

Due to constant pressure  $dp = 0$  hence  $dq = dh$

Hence:  $c_p = \left[ \frac{dh}{dT} \right]_p$

In a general change  $dh = \left[ \frac{\partial h}{\partial T} \right]_p dT + \left[ \frac{\partial h}{\partial p} \right]_T dp$

../continued

# The First Law of Thermodynamics

Constant pressure specific heat

For **ideal gases**,  $u$  is a function of  $T$  only,  
and also  $pv = RT$  is a function of  $T$  only

$h = u + pv$  is a function of  $T$  only, hence  $\left[\frac{\partial h}{\partial p}\right]_T = 0$

Thus  $dh = c_p dT$

For gases with constant  $c_p$   $\Delta h = h_2 - h_1 = c_p (T_2 - T_1)$

For **an ideal gas**,  $h = u + p.v = u + RT$

$$\frac{dh}{dT} = \frac{du}{dT} + R \quad \rightarrow \quad c_p = c_V + R \quad \text{or} \quad \underline{c_p - c_V = R}$$

$$c_p = \frac{dh}{dT}$$

# The First Law of Thermodynamics

## Heat capacities

### For gases

	$c_V$	$c_p$	Note
By definition	$c_V = \left[ \frac{dq}{dT} \right]_V$	$c_p = \left[ \frac{dq}{dT} \right]_p$	For specific processes (constant V or constant p), but any substance
By derivation	$c_V = \frac{du}{dt}$	$c_p = \frac{dh}{dt}$	For any processes (not just constant V or constant p), but ideal gases only

$$c_p - c_V = R$$

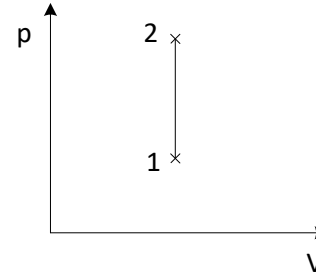
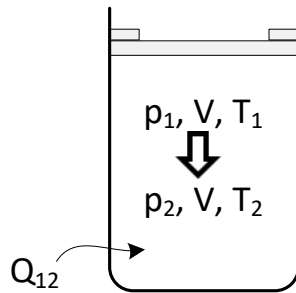
### For liquids and solid

$$c_V \approx c_p \approx c$$

$$dh \approx du \approx c dT$$

# Typical gas processes for closed systems

## Isochoric (constant volume) process



Work done during the process:

$$W_{12} = \int_1^2 p dV = 0$$

Heat transfer during the process

$$dQ = dU = mc_V dT$$

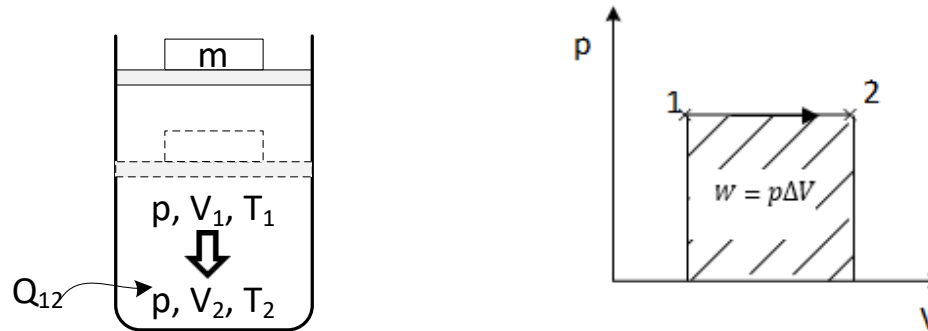
For gases with constant  $c_v$

$$Q_{12} = \Delta U_{12} = mc_V(T_2 - T_1)$$



# Typical gas processes for closed systems

Isobaric (constant pressure) process



Work done in process:

$$W_{12} = \int_1^2 p dV = \underline{p(V_2 - V_1)}$$

Heat transfer in process:

$$dQ = mc_p dT$$

For gases with constant  $c_p$

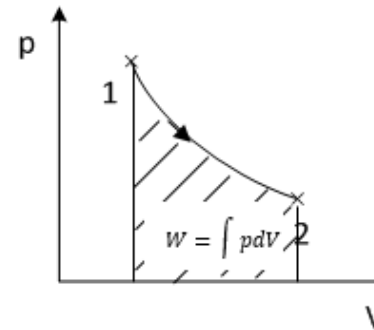
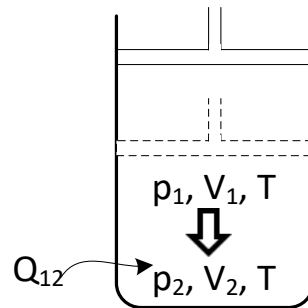
$$Q_{12} = mc_p(T_2 - T_1)$$

For any gases, from the First Law

$$Q_{12} = U_2 - U_1 + p(V_2 - V_1) = (U_2 + pV_2) - (U_1 + pV_1) = H_2 - H_1 = m(h_2 - h_1)$$

# Typical gas processes for closed systems

## Isothermal (constant temperature) process



Work done during the process:

$$W_{12} = \int_1^2 p dV$$

For an **ideal gas**:

$$p_1 V_1 = p_2 V_2 = mRT$$

$$W_{12} = \int_1^2 \frac{mRT}{V} dV = mRT \int_1^2 \frac{1}{V} dV = \underline{p_1 V_1 \ln(V_2/V_1)} = p_2 V_2 \ln \frac{V_2}{V_1}$$

Heat transfer during the process

$$\Delta U = mc_V \Delta T = 0$$

Heat transfer

$$Q_{12} = W_{12} + \Delta U = W_{12} + 0 = p_1 V_1 \ln(V_2/V_1)$$

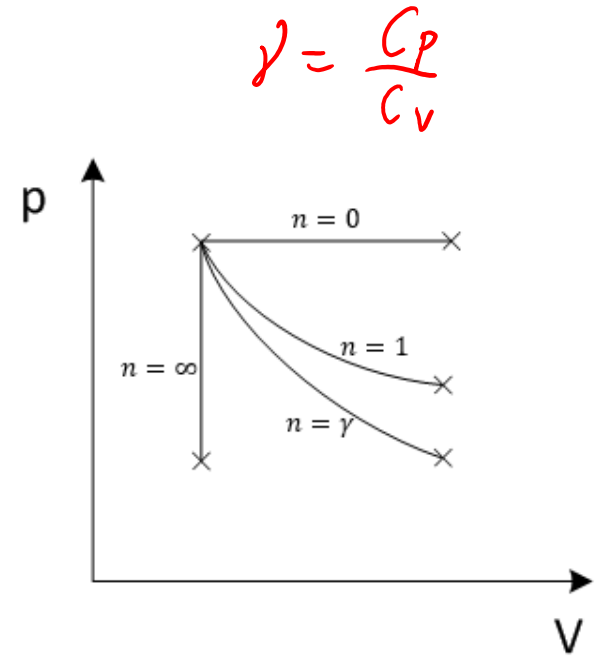
# Typical gas processes for closed systems

## Polytropic process

Many real processes follow relationships of the form  
 $pV^n = \text{constant}$  or  $pV^{(n)} = \text{constant}$   
 for  $1 \leq n \leq \gamma$  ( $\gamma$  is the ratio of sp heats  $\gamma = \frac{c_p}{c_v}$ )

For an **ideal gas**, alternative ways of expressing the  
 Polytropic relationship from  $pV^n = C$ :

$$TV^{(n-1)} = C \quad \text{or} \quad pT^{-n/(n-1)} = C$$



## Work done in process

$$W_{12} = \int_1^2 p dV = C \int_1^2 \frac{1}{V^n} dV = \frac{C}{1-n} \left[ \frac{1}{V^{n-1}} \right]_1^2 = \frac{1}{1-n} \left[ \frac{p_2 V_2^n}{V_2^{n-1}} - \frac{p_1 V_1^n}{V_1^{n-1}} \right] = \frac{p_2 V_2 - p_1 V_1}{1-n}$$

Internal energy change:

$$\Delta U = mc_V(T_2 - T_1)$$

Heat transfer:

$$Q_{12} = \Delta U + W_{12}$$

$W = p_1 V_1 \ln \frac{V_2}{V_1}$

# Typical gas processes for closed systems

Reversible adiabatic (Isentropic) process

An **adiabatic** process is one in which no heat crosses the system boundary.

For a reversible adiabatic process, according to definition,

$$Q_{12} = 0$$

Hence work done in process

$$W_{12} = -(U_2 - U_1)$$

From the First Law, for gases with constant specific heat

$$dq - pdv = du = c_V dT$$

For adiabatic processes

$$dq = 0$$

Hence

$$-pdv = c_V dT$$

For an ideal gas

$$pv = RT$$

Substituting

$$-\frac{dv}{v} = \frac{c_V dT}{RT} \quad \text{where} \quad R = c_p - c_V$$

Define heat capacity ratio

$$\gamma = \frac{c_p}{c_V}, \quad \text{then} \quad R = c_p - c_V = (\gamma - 1)c_V$$

Substituting

$$-\ln v = \frac{1}{\gamma - 1} \ln T + \text{const.}$$

$$(\gamma - 1) \ln v + \ln T = \text{const.}$$

$$Tv^{\gamma-1} = \text{const.}$$

Or from the equation of states

$$pv^\gamma = \text{const.}$$

For dry air, we can usually use  $\gamma = 1.4$

*Isentropic*

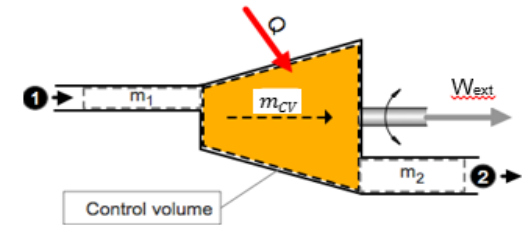
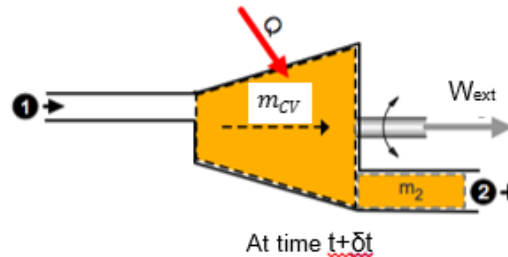
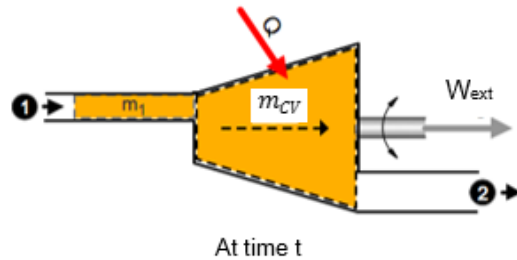
Adiabatic  $\neq$  Isothermal

# Steady Flow Energy Equation (SFEE)

General continuity equation for a constant volume system

General continuity equation for a constant volume system

$$0 = \frac{\partial m_{CV}}{\partial t} + \dot{m}_{out} - \dot{m}_{in}$$



**Boundary work** =  $\int p dV \cong m p v$

**Work ...**  $W = W_S + m_2 p_2 v_2 - m_1 p_1 v_1$

**Energy ...**  $E_2 - E_1 = (E_{CV2} + m_2 e_2) - (E_{CV1} + m_1 e_1)$

Applied the First Law

$$Q - (W_{ext} + m_2 p_2 v_2 - m_1 p_1 v_1) \\ = \left[ E_{CV2} + m_2 \left( u_2 + \frac{1}{2} c_2^2 + g z_2 \right) \right] - \left[ E_{CV1} + m_1 \left( u_1 + \frac{1}{2} c_1^2 + g z_1 \right) \right]$$

BUT  $m_1 = m_2 = m$  and on average  $E_{CV2} = E_{CV1}$

$$Q - W_{ext} = m \left[ \underbrace{(p_2 v_2 + u_2)}_{h_2} + \frac{1}{2} c_2^2 + g z_2 \right] - \left[ \underbrace{(p_1 v_1 + u_1)}_{h_1} + \frac{1}{2} c_1^2 + g z_1 \right]$$

SFEE

$$\dot{Q} - \dot{W}_{ext} = \dot{m} \left[ \left( h_2 + \frac{1}{2} c_2^2 + g z_2 \right) - \left( h_1 + \frac{1}{2} c_1^2 + g z_1 \right) \right]$$

$$\dot{Q} - \dot{W}_{ext} = \dot{m} (h_2 - h_1)$$

## External work

External work (or useful work) is separated from the work done at the boundaries. i.e. flow work  $p_2 v_2 - p_1 v_1$

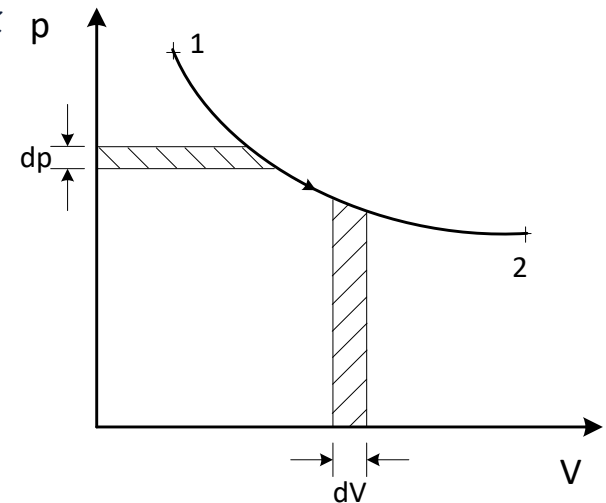
For the flow process  $w_{ext} = \text{total work} - \text{flow work}$

$$= w + (pv)_1 - (pv)_2$$

$$= \int_1^2 p dv + p_1 v_1 - p_2 v_2$$

$$= - \int_1^2 v dp$$

$$w = \int_1^2 p dv$$



Process	Non-flow work done	Steady flow work done	"flow work"
$v=\text{const}$	0	$-v(p_2 - p_1)$	$v(p_2 - p_1)$
$p=\text{const}$	$p(v_2 - v_1)$	0	$p(v_2 - v_1)$
$pv^n=\text{const}$	$\frac{p_2 v_2 - p_1 v_1}{1 - n}$	$\frac{n(p_2 v_2 - p_1 v_1)}{1 - n}$	$(p_2 v_2 - p_1 v_1)$

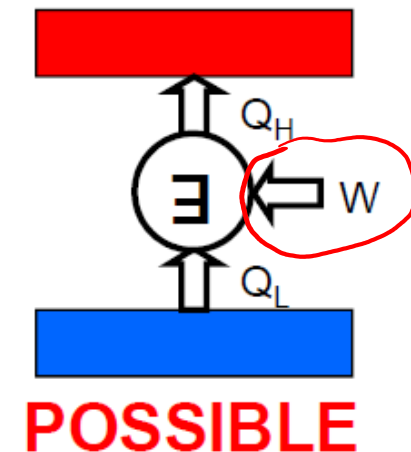
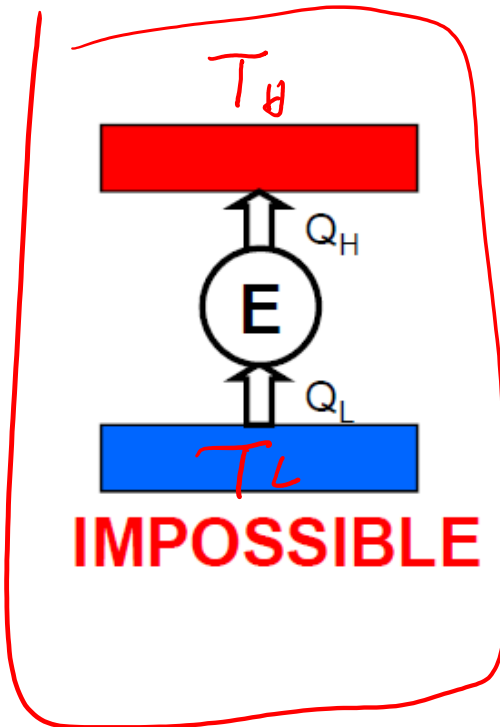




# The Second Law of Thermodynamics

## Clausius Statement

The Clausius statement of the second law states that no device can transfer heat from a cooler body to a warmer one **without leaving an effect on the surroundings**.

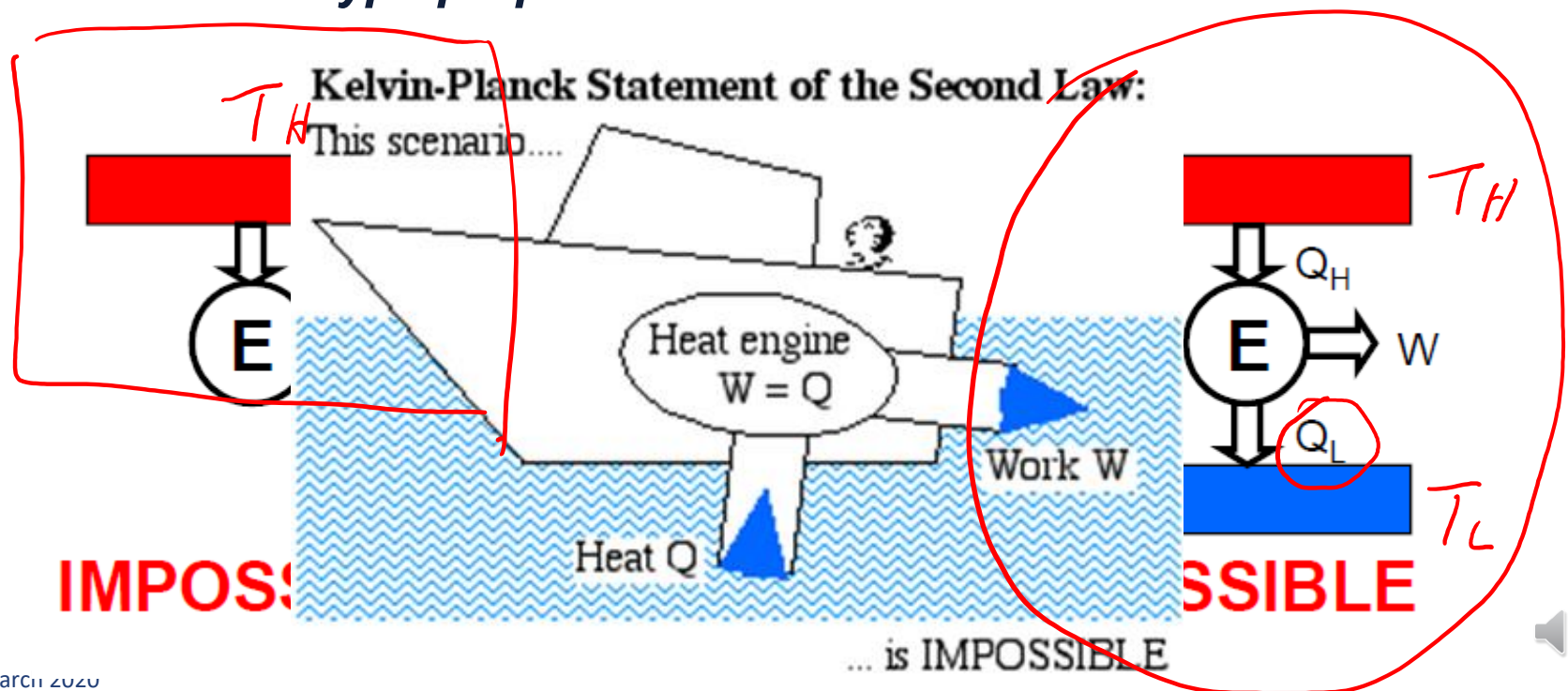


# The Second Law of Thermodynamics

## Kelvin-Planck Statement

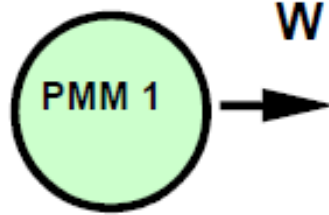
The Kelvin -Planck statement of the second law of thermodynamics states that no heat engine can produce a net amount of work while exchanging heat with a **single reservoir only**.

Any device that violates the first or the second law of thermodynamics is called a **second type perpetual-motion machine**.

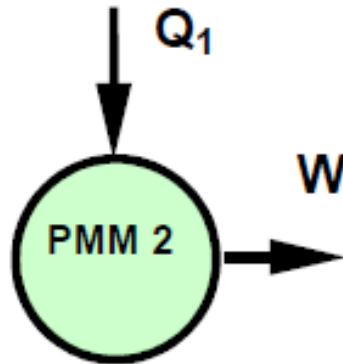


# The Second Law of Thermodynamics

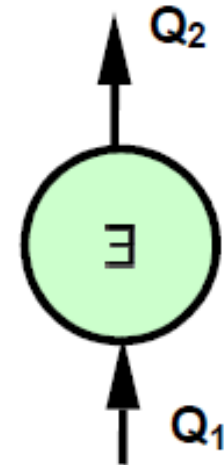
Summary of possible and impossible heat engines



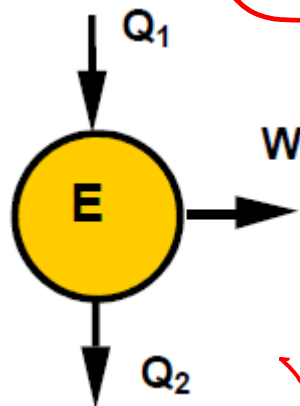
Impossible  
(1<sup>st</sup> Law)



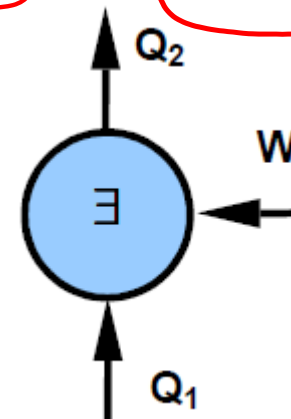
Impossible  
(2<sup>nd</sup> Law KP statement)



Impossible  
(2<sup>nd</sup> Law Clausius statement)

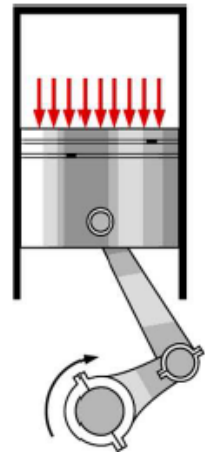
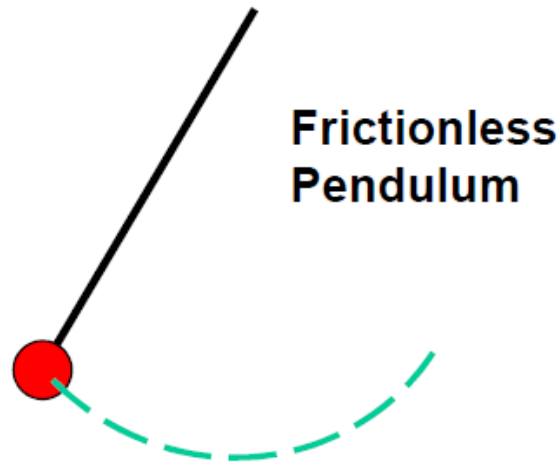


Possible  
(Heat engine)

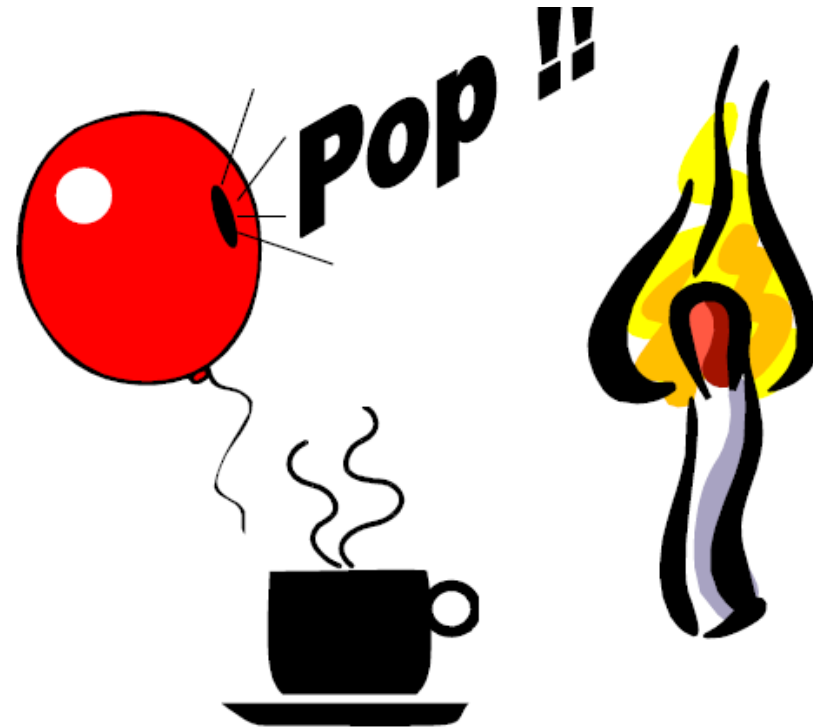


Possible  
(reversed heat engine)

# Reversible and Irreversible processes



Quasi-  
equilibrium  
expansion  
and  
compression  
of a gas



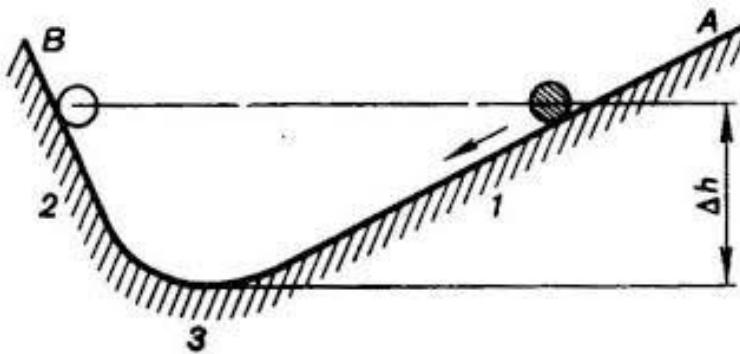
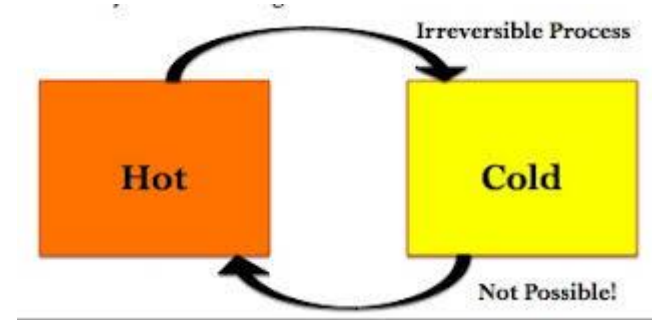
## Reversible Process:

A process which can be reversed without leaving any trace on the surroundings

# Reversible and irreversible processes

## Causes of Irreversibility

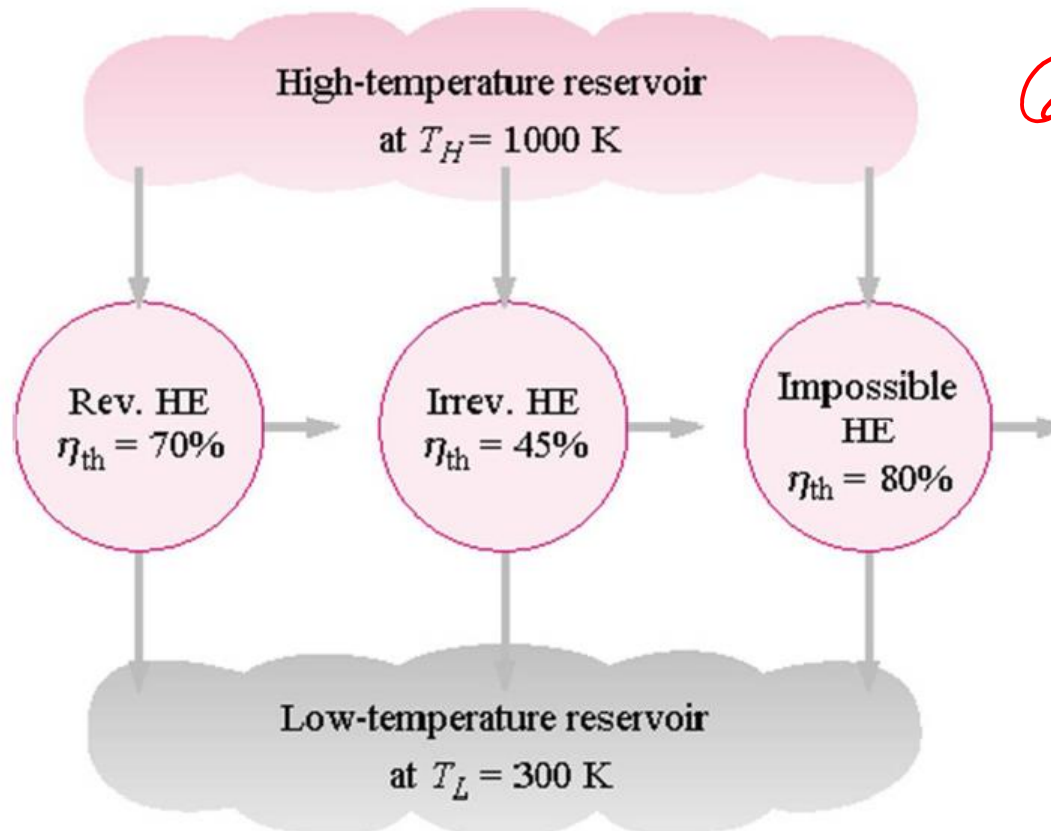
- Friction
- Heat transfer
- Non-quasi-equilibrium processes  
i.e. rapid compression/expansion
- Mixing



# Reversible heat engine

The most efficient (imaginary) engine between the same high and low temperature reservoirs

No heat engine can have a higher efficiency than a **Reversible heat engine** operating between the same high- and low- temperature reservoirs

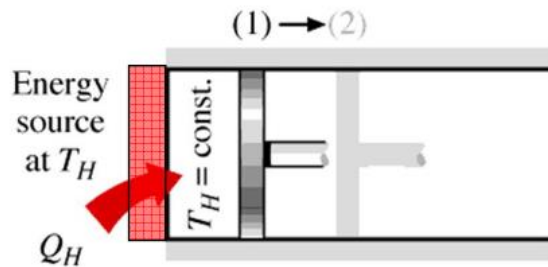


*Carnot*

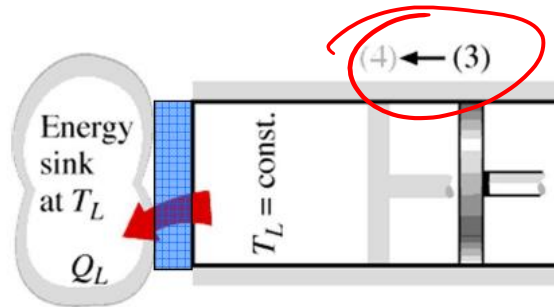
$$\eta_{Carnot} = 1 - \frac{T_L}{T_H}$$

$$\eta_{Carnot} = 1 - \frac{300}{1000} = 70\%$$

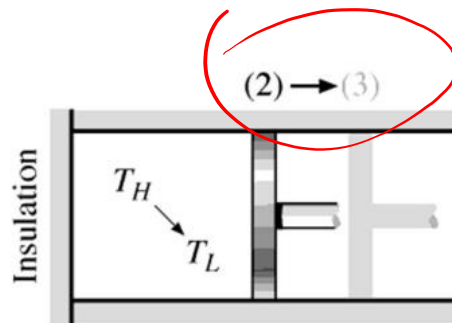
# Carnot cycle



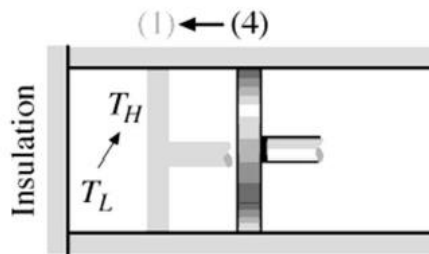
(a) Process 1-2



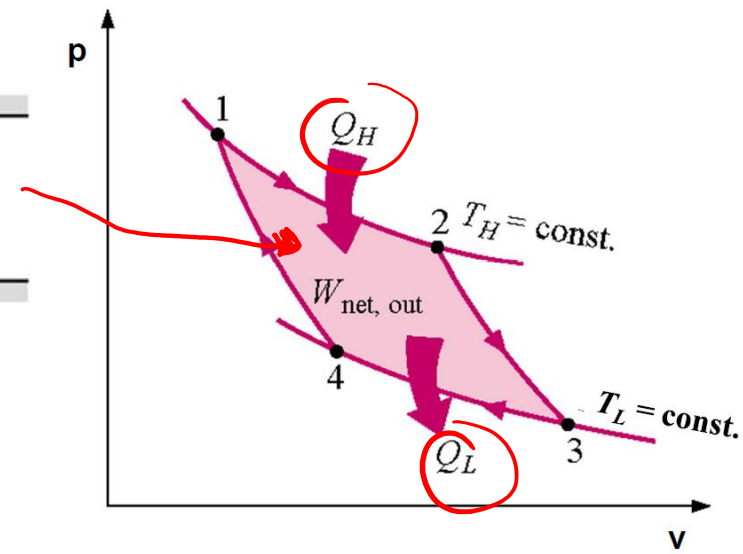
(c) Process 3-4



(b) Process 2-3



(d) Process 4-1



Reversible heat engine

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$$

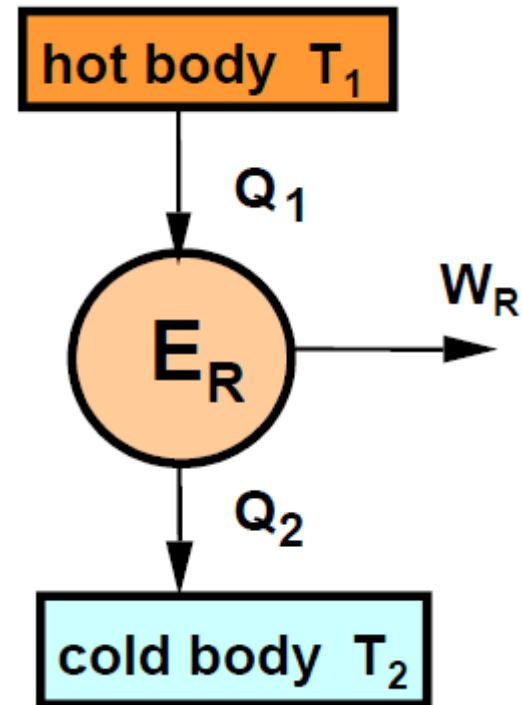
or

$$\oint \frac{dQ_R}{T} = 0$$

$$\int \frac{dQ_R}{T} = \text{property change} = \underline{S_1 - S_2}$$

**S=entropy (kJ/K)**

**Or  $s=S/m$ =specific entropy (kJ/kg K)**





# Entropy change and T-s diagram

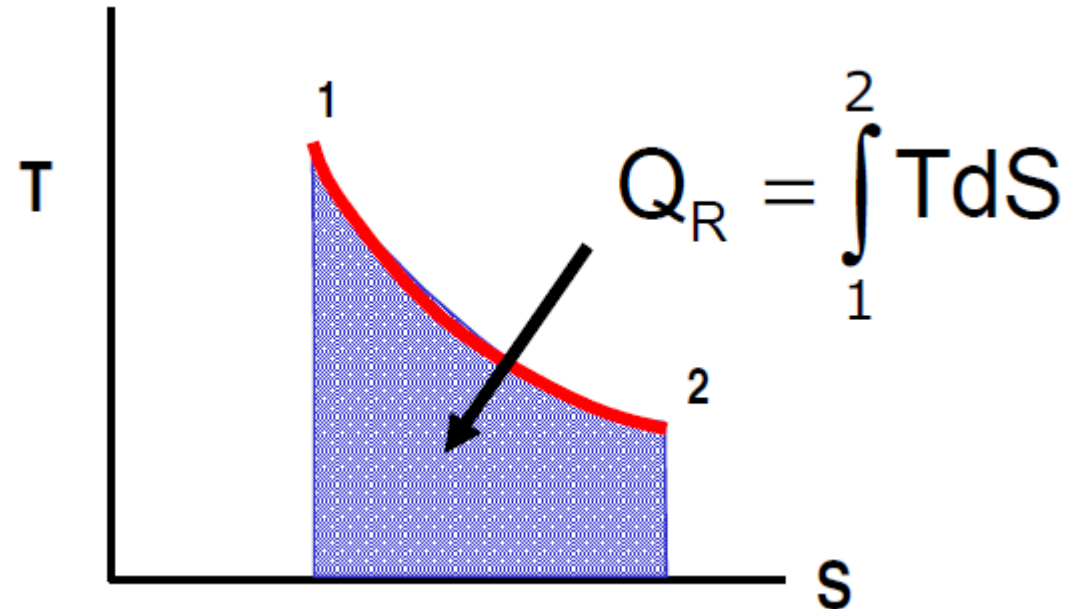
Chosen T-s diagram as

$$dq = Tds$$

Isentropic process

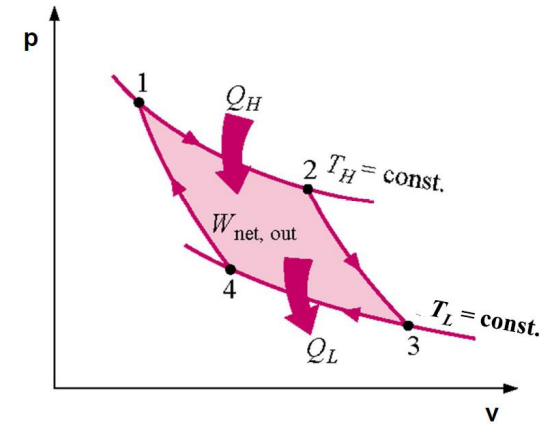
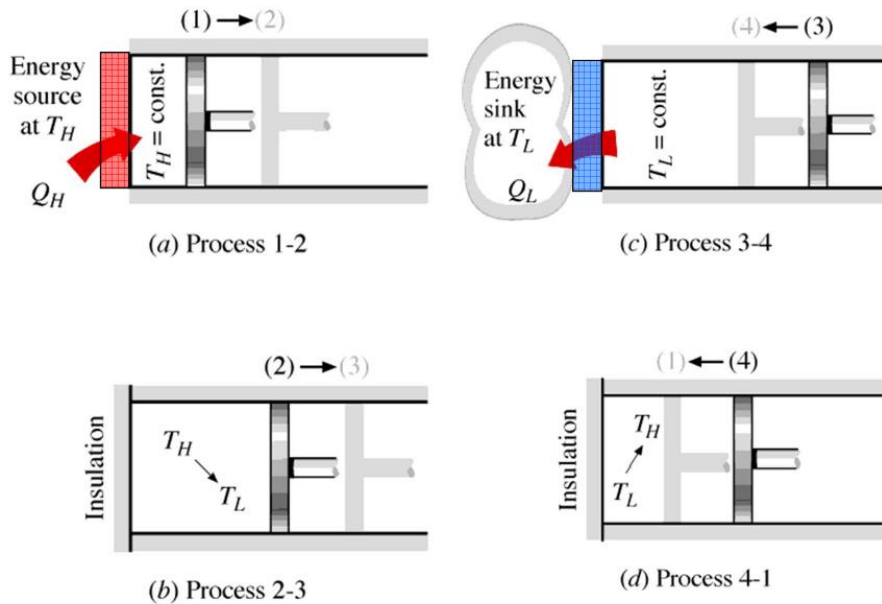
Entropy change = 0

$$\int \frac{dQ_R}{T} = 0$$

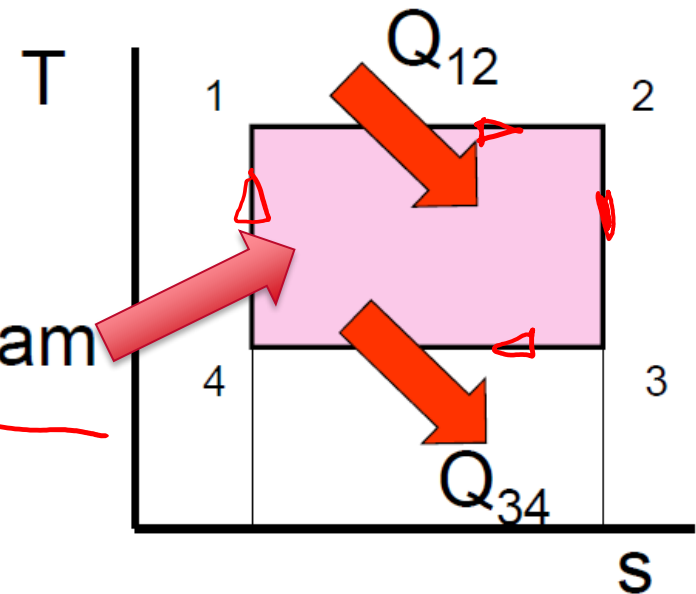


Isentropic = Adiabatic + Reversible

# Revisit Carnot Cycle



$$\underline{W_{\text{net}}} = \underline{\sum Q} = \underline{\text{area of T-s diagram}}$$



# Principle of increase of entropy

Consider two heat engines between same heat reservoirs:  
a reversible and an irreversible

$$\eta_R \geq \eta_I$$

For the reversible engine, we have

$$\eta_R = 1 - \frac{T_L}{T_H}$$

For the irreversible engine, we have

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

Therefore

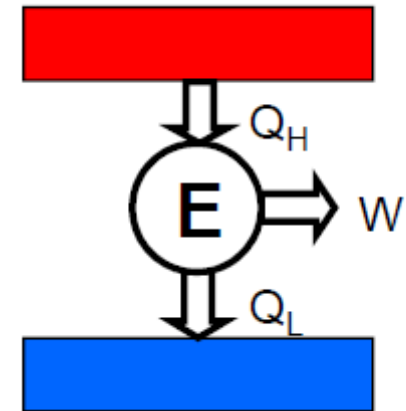
$$\frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} \leq \frac{T_H - T_L}{T_H}$$

Rearrange

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} \leq 0$$

or in general

$$\oint \frac{dQ}{T} \leq 0$$



$$\oint \frac{dQ_R}{T} = 0$$

The definition of entropy is based on the Clausius inequality, given by

$$\oint \frac{dQ}{T} \leq 0 \quad (kJ / K)$$

---

where the equality holds for internally or totally reversible processes and the inequality for irreversible processes.

Consider a system that undergoes a cycle comprising an irreversible adiabatic process (1a2) and a reversible process (2b1)

For the **adiabatic** process (1a2)

$$\int_1^2 \left( \frac{dq}{T} \right)_a = 0$$

But irreversible

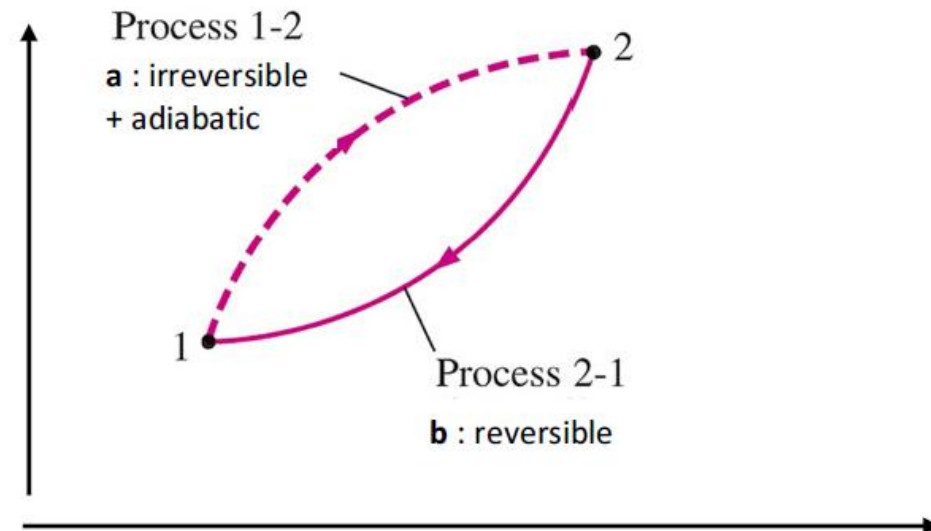
$$\int_1^2 \left( \frac{dq}{T} \right)_a \neq \int_1^2 ds$$

For the **reversible** process (2b1)

$$\int_2^1 \left( \frac{dq}{T} \right)_b = s_1 - s_2$$

Clausius inequality  $\oint \frac{dQ}{T} \leq 0$

Therefore  $\int_1^2 \left( \frac{dq}{T} \right)_a + \int_2^1 \left( \frac{dq}{T} \right)_b = 0 + (s_1 - s_2) \leq 0 \Rightarrow s_2 \geq s_1$



# Entropy generation



Entropy always increases!!!

The inequality part of the Clausius inequality combined with the definition of entropy yields an inequality known as the ***increase of entropy principle***, expressed as

$$S_{gen} \geq 0 \quad (kJ / K)$$

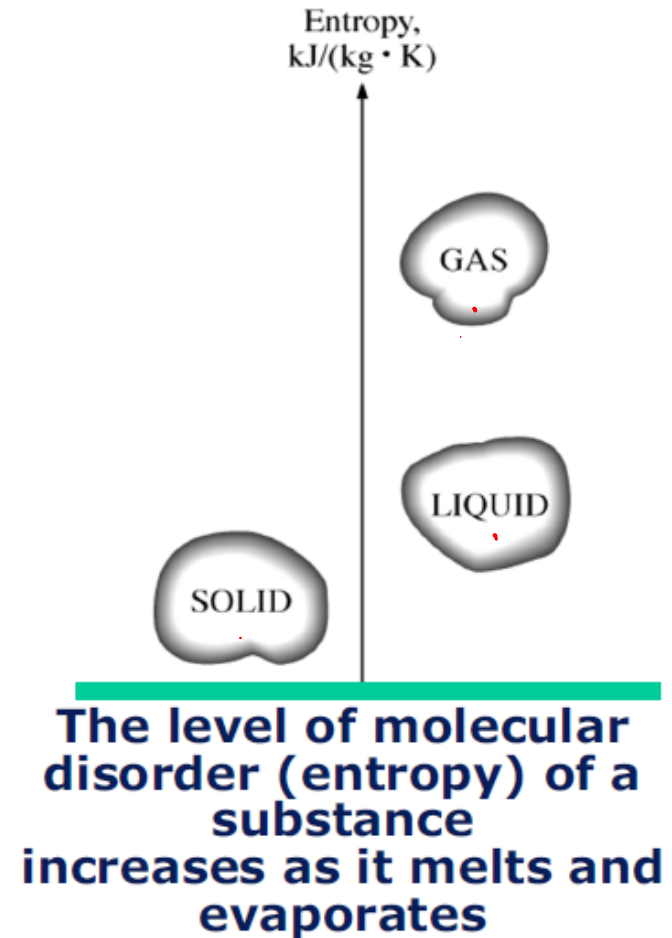
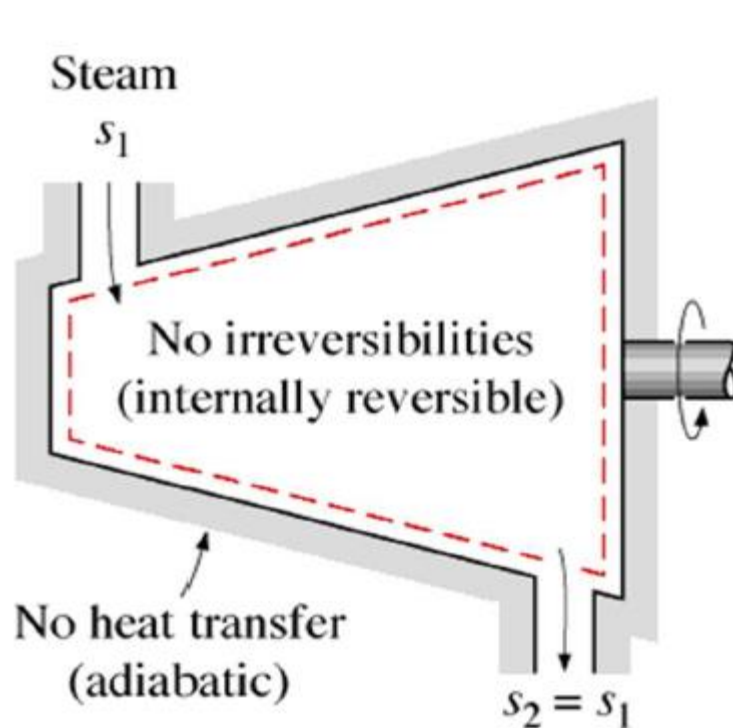
Where  $S_{gen}$  is the entropy generated during a process.

$$\boxed{dS = \frac{dQ_R}{T}} \quad \text{or} \quad \boxed{dS = \frac{dQ}{T} + S_{gen}}$$

 **Reversible process**                       **Irreversible process**

# What is entropy?

Entropy: a measure of **DISORDER**



The entropy-change for a process involving an ideal gas can be summarized as follows:

$$s_2 - s_1 = c_V \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{v_2}{v_1} \right)$$

And

$$s_2 - s_1 = c_p \ln \left( \frac{T_2}{T_1} \right) - R \ln \left( \frac{p_2}{p_1} \right)$$

For liquid or solid, as  $v_2 \approx v_1$

$$s_2 - s_1 = c_V \ln \left( \frac{T_2}{T_1} \right)$$



# Derivation of T-ds relations

$$\begin{aligned}h &= u + pv \\dh &= du + pdv + vdp \\ds &= \frac{dq_r}{T}\end{aligned}$$

First Law:

$$dq_r = du + pdv$$

Hence:

$$Tds = du + pdv = dh - vdp$$

For an ideal gas:

$$c_V = \frac{du}{dT} \qquad c_p = \frac{dh}{dT}$$

Therefore:

$$Tds = du + pdv = c_V dT + pdv$$

And

$$ds = c_V \frac{dT}{T} + p \frac{dv}{T} = c_V \frac{dT}{T} + \frac{R}{v} dv \quad (\text{with } pv = RT)$$

Hence:

$$\int_1^2 ds = c_V \int_1^2 \frac{dT}{T} + R \int_1^2 \frac{dv}{v}$$

Hence:

$$s_2 - s_1 = c_V \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{v_2}{v_1} \right)$$

Derive:

$$s_2 - s_1 = c_p \ln \left( \frac{T_2}{T_1} \right) - R \ln \left( \frac{p_2}{p_1} \right)$$