specific Heat

In considering heat interactions with the gas we must consider the heat capacity of the gas.

DEFINITION:

Heat capacity — amount of heat required to raise the temperature of a substance.

$$C = \frac{Q}{\Delta T}$$

Q ← heat

ΔT ← temperature difference

C ↑ heat capacity

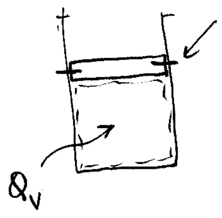
specific heat $c = \frac{C}{m}$ ← mass

specific heat — amount of heat required to raise the temperature of a unit mass of a substance by one degree

$$c \equiv \frac{1}{m}\frac{\delta Q}{dT}$$

For a gas a different amount of heat is required if the process occurs at a constant volume or a constant pressure

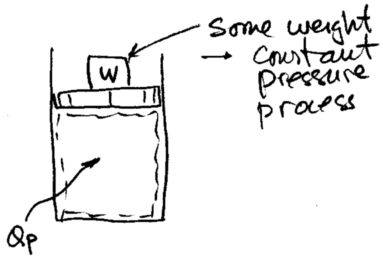
specific heat at constant volume



pin → constant volume process

$$c_v \equiv \frac{1}{m}\frac{\delta Q_v}{dT}$$

Specific heat at constant pressure



$$c_p \equiv \frac{1}{m}\frac{\delta Q_p}{dT}$$

Differential form of the 1st Law:

$$dU = \delta Q - \delta W$$

Compression - expansion work in a closed system

$$\delta W = m p\, dv$$

Hence

$$dU = \delta Q - m p\, dv$$
$$\delta Q = dU + m p\, dv$$

For a constant volume process $v = \text{const}$ and $dv = 0$

$$(\delta Q)_v = dU = m\, du$$

and $c_v = \frac{1}{m}\frac{(\delta Q)_v}{dT} \rightarrow (\delta Q)_v = m c_v dT$

$$\underline{c_v = \frac{du}{dT}}$$

NOTE ① This an expression for c_v in terms of state variables, u and T.
② c_v is a property of the substance.

$$du = c_v dT$$

This equation can be integrated

$$\Delta u = \int_1^2 du = \int_1^2 c_v dT$$

In general c_v is a function of temperature. For c_v = constant

$$\underline{\Delta u = c_v \Delta T}$$

For a constant pressure process

$$c_p \equiv \frac{1}{m}\frac{(\delta Q)_p}{dT}$$

For compression–expansion work, 1st Law:

$$\delta Q = dU + m\,p\,dv$$

We define a new function, called ENTHALPY

$$H \equiv U + pV$$ ← extensive variables

$$h = u + pv$$ ← intensive variables (h is a state variable)

$$dh = du + p\,dv + v\,dp$$

$$du = dh - p\,dv - v\,dp$$

$$\frac{\delta Q}{m} = (dh - \cancel{p\,dv} - v\,dp) + \cancel{p\,dv}$$

$$\frac{\delta Q}{m} = dh - v\,dp$$

Now, for a constant pressure process $p = \text{constant}$, $dp = 0$

$$\left(\frac{\delta Q}{m}\right)_p = dh$$

and $$\underline{c_p \equiv \frac{dh}{dT}}$$

<u>NOTE:</u> ① This is an expression for c_p in terms of state variables, h and T
② c_p is a property of the substance

$$dh = c_p\,dT$$

This equation can be integrated:

$$\Delta h = \int_1^2 dh = \int_1^2 c_p\,dT$$

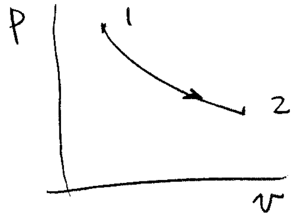
In general c_p is a function of temperature,

For $c_p = \text{constant}$

$$\underline{\Delta h = c_p\,\Delta T}$$

Return to the 1st Law statement for a process

$\Delta U = Q - W$ for a closed system



We have shown that

$$W_{12} = m\int_1^2 p\,dv$$

We have just demostrated

$$du = c_v\,dT$$

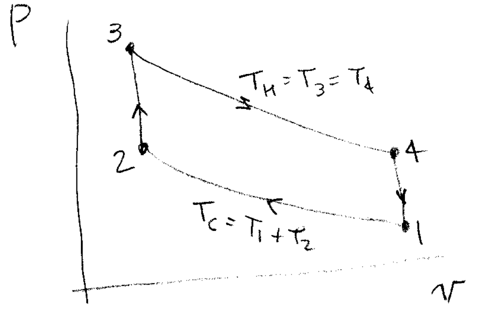
hence $\Delta U_{12} = m\int_1^2 c_v\,dT$ note $U = mu$

$= mc_v(T_2 - T_1)$ for c_v = constant.

We can now evaluate the heat transfer, Q, for the process

$$Q_{12} = \Delta U_{12} + W_{12} = m\int_1^2 c_v\,dT + m\int_1^2 p\,dv$$

Return to the Stirling cycle,



Renumbe the states so that the initial state will correspond to the ambient conditions, typically $T_0 = 300K$ & $p = 100$ kPa

Process 1-2: Constant temperature (isothermal) compression

Process 2-3: Constant volume (isochoric, isometric) compression

Process 3-4: Constant temperature (isothermal) expansion

Process 4-1: Constant volume (isochoric, isometric) expansion

Consider now each of the four processes.

$\boxed{\text{Process 1-2}}$ – isothermal compression, $T_1 = T_2$

State 1 state variables: p_1, v_1, T_1 (pvT-state variables)

Relationship among these state variables is called an equation of state and is given by the ideal gas law $pv = RT$ ($pV = mRT$, $pV = n\bar{R}T$)

Gas constant

universal Gas constant

no. of moles

Hence:

$$p_1 v_1 = RT_1$$

State 2 state variables are p_2, v_2, T_2

and $$p_2 v_2 = RT_2$$

Process 1-2 equation: from $T_1 = T_2$ and the equation of state (ideal gas equation), $pv = RT$, we have:

$$pv = RT_1 = RT_2 = \text{constant} \quad \text{(for process 1-2 only)}$$

We can now evaluate the work for this process:

$$\frac{W_{12}}{m} = \int_1^2 p\, dv$$

Substitute for p from the process 1-2 equation.

$$p = \frac{RT_1}{v}$$

$$\frac{W_{12}}{m} = w_{12} = \int_1^2 \frac{RT_1}{v}\, dv = RT_1 \int_1^2 \frac{dv}{v} = RT_1 \int_1^2 d(\ln v)$$

$$\underline{w_{12} = RT_1 \ln \frac{v_2}{v_1}}$$

The change in internal energy for this process is (assuming c_v = constant, actually $c_v = f(T)$)

$$\Delta U_{12} = \int_1^2 m c_v\, dT = c_v m \int_1^2 dT = m c_v (T_2 - T_1)$$

$$\underline{\frac{\Delta U_{12}}{m} = \Delta u_{12} = c_v (T_2 - T_1) = 0} \quad \text{since } T_2 = T_1$$

We can now evaluate the heat transfer for this process from the 1st Law of Thermo expression

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

$$\frac{Q_{12}}{m} = q_{12} = c_v(T_2 - T_1) + RT_1 \ln\frac{v_2}{v_1} = 0 + RT_1 \ln\frac{v_2}{v_1}$$

$$\underline{q_{12} = w_{12} = RT_1 \ln\frac{v_2}{v_1}}$$

Thus far we have analytical relations among the variables: Consider the mathematics for the solution of this problem:

<u>VARIABLES</u>: $p_1, v_1, T_1, p_2, v_2, T_2, \Delta u_{12}, q_{12}, w_{12}$

We have nine (9) variables

<u>EQUATIONS</u>: $\underline{p_1 v_1 = RT_1}$, $p_2 v_2 = RT_2$

From $T_1 = T_2$ we get $pv = RT_1 = RT_2$ = constant, hence $\underline{p_2 v_2 = p_1 v_1}$

$\underline{\Delta u_{12} = 0}$, $\underline{w_{12} = RT_1 \ln\frac{v_2}{v_1}}$, $\underline{q_{12} = w_{12}}$

We have six (6) equations.

To solve this process we must specify 3 independent ⊛ variables. Note that specifying p_1, v_1 and T_1 will not solve the problem, since these three variables are not independent. We must choos 3 independent variables.

Here are some possibilities:

- T_1, p_1, v_2
- T_1, p_1, p_2
- T_1, p_1, w_{12}
- etc.

⊛ <u>NOTE</u>: If we specify p_1, v_1 & T_1 we will have 6 var. and <u>5</u> equations since the equation $p_1 v_1 = RT_1$ does not contribute to the set of equation. Hence we still need to specify one more variable

If we specify, T_1, p_1 and v_2 we obtain

$$v_1 = \frac{RT_1}{p_1}, \quad p_2 = \frac{p_1 v_1}{v_2},$$

$$w_{12} = RT_1 \ln \frac{v_2}{v_1}, \quad q_{12} = w_{12}$$

$\boxed{\text{PROCESS 2-3}}$ Constant volume compression $V_3 = V_2$

State 2 variables are p_2, v_2, T_2

State 3, the variables are p_3, v_3, T_3

Process 2-3 equation. From $V_3 = V_2$ or $v_3 = v_2$ and the equation of state $pv = RT$, we have

$$\frac{p_2}{T_2} = \frac{p_3}{T_3}$$

Calculate next the process variables, w_{12}, Δu_{12}, q_{12}

WORK

$$\frac{W_{23}}{m} = w_{23} = \int_2^3 p\,dv, \quad \text{but } dv = 0, \text{ hence } \underline{w_{23} = 0}$$

Δ INTERNAL ENERGY

$$\frac{\Delta U_{23}}{m} = \Delta u_{23} = \int_2^3 c_v\,dT = c_v \int_2^3 dT \Rightarrow \underline{\Delta u_{23} = c_v(T_3 - T_2)}$$

HEAT

$$Q_{23} = \Delta U_{23} + W_{23} = \Delta U_{23} \Rightarrow \underline{q_{23} = \Delta u_{23} = c_v(T_3 - T_2)}$$

To solve this process, consider the variables and the equations.

VARIABLES: $p_2, v_2, T_2, p_3, v_3, T_3, w_{23}, \Delta u_{23}, q_{23}$.

EQUATIONS: $p_2 v_2 = RT_2$, $p_3 v_3 = RT_3$, $\frac{p_2}{T_2} = \frac{p_3}{T_3}$

$w_{23} = 0$, $\Delta u_{23} = c_v(T_3 - T_2)$, $q_{23} = \Delta u_{23}$

We again have 9 variables and 6 equation. We must specify 3 independent variable. If we started with state 1 and process 1-2, state 2 would have become known, i.e, p_2, v_2, T_2 would be known. Hence we now have 6 variables and 5 equations, since the equation $p_2 v_2 = RT_2$ is no longer an independent equation.

To complete the process calculation, we must specify one more independent variable. The additional variable can come from one of the state 3 state variables, such as the maximum cycle temperature T_3, or one of the process 2-3 variables, such as Q_{23}.

PROCESS 3-4 Isothermal expansion, $T_4 = T_3$

State 3 variables; p_3, v_3, T_3

State 4 variables: p_4, v_4, T_4

Process 3-4 equation: From $T_4 = T_3$ and $pv = RT$, we have

$pv = RT_3 =$ constant. $\quad p = \dfrac{RT_3}{v}$

Evaluation of: WORK: $W_{34}/m = \int_3^4 p\,dv = RT_3 \int_3^4 \frac{dv}{v} = \underline{RT_3 \ln \frac{v_4}{v_3}}$

$\Delta U_{34}/m = \Delta u_{34} = c_v(T_4 - T_3) \underline{= 0}$

HEAT $\quad Q_{34} = \Delta U_{34} + W_{34} \rightarrow q_{34} = \cancel{\Delta u_{34}}^{0} + w_{34} \rightarrow \underline{q_{34} = w_{34}} = RT_3 \ln \frac{v_4}{v_3}$

Solution: If state 3 has been evaluated, we again will have 6 variables and 5 equations as above, and will have to specife one more independent variable. This independent variable in this case will be v_4. This information is obtained from Process 4-1, that specifies a constant volume expansion and $v_4 = v_1$. Hence v_4 will be the additional variable.

PROCESS 4-1 Constant volume expansion $V_4 = V_1$, $v_4 = v_1$

State 4 variables p_4, v_4, T_4

State 1 variables p_1, v_1, T_1

Process 4-1 equation from $v_4 = v_1$ and $pv = RT$ we have

$$\frac{p_4}{T_4} = \frac{p_1}{T_1}$$

Calculation of the process variables:

$w_{41} = \int_4^1 p\,dv = 0$ since $dv = 0$

$\Delta u_{41} = c_v(T_1 - T_4)$, $\quad q_{41} = \Delta u_{41} + \cancel{w_{41}}^{0} = \Delta u_{41} = c_v(T_1 - T_4)$

Solution. If we are calculating process 4-1, beginning with the initial state, state 1, we now know all the state variables, in particular the following are known: p_4, v_4, T_4, p_1, v_1, and T_1. We are now left with 3 unknowns; Δu_{23}, w_{23}, and q_{23}, and with 3 equations: Thus, the fourth cycle, cycle 4-1 is solved.

Summary of process calcutation

We have calculated each of the four process that make up the Stirling cycle and can now proceed to the calculation of the cycle as a whole.

Note that in order to complete the calculations, it was necessary to specify four independent variable. There are several combinations possible. For example: the initial pressure and temperature, p_1 and T_1, the specific volume v_2, and the maximum cycle temperature, T_3.

CYCLE CALCULATION

There are three quantities of primary interest:

- Net work of the cycle
- Heat Intut to the cycle
- Thermal efficiency of the cycle.

Net work of the cycle

The net work of the cycle is the sum of the work of each cycle

$$W_{net} = \sum W_i = W_{12} + W_{23} + W_{34} + W_{41}$$

$$\frac{W_{net}}{m} = RT_1 \ln \frac{v_2}{v_1} + 0 + RT_3 \ln \frac{v_4}{v_3} + 0$$

Recall that $v_3 = v_2$ and $v_4 = v_1$, also $v_1 > v_2$

$$w_{net} = RT_1 \ln \frac{v_2}{v_1} + RT_3 \ln \frac{v_1}{v_2} = -RT_1 \ln \frac{v_1}{v_2} + RT_3 \ln \frac{v_1}{v_2}$$

$$\underline{w_{net} = R(T_3 - T_1) \ln \frac{v_1}{v_2}} \quad \blacktriangleleft$$

since $v_1/v_2 > 1$ and $T_3 > T_1$, $w_{net} > 0$, indicating a net positive work output of the cycle according to our sign convention. Positive work represents work output, and a negative value represents work input.

Heat input to the cycle

According to our sign convention, positive values of heat represent heat input, and negative values represent heat output. We thus must examine the sign of the heat transfer for each process.

Process 1–2: $q_{12} = RT_1 \ln \frac{v_2}{v_1} = -RT_1 \ln \frac{v_1}{v_2}$ ⇨ heat output

Process 2–3: $q_{23} = c_v(T_3 - T_2) = c_v(T_3 - T_1)$ ⇨ heat input

Process 3–4: $q_{34} = RT_3 \ln \frac{v_4}{v_3} = RT_3 \ln \frac{v_1}{v_2}$ ⇨ heat input

Process 4–1: $q_{41} = c_v(T_1 - T_4) = -c_v(T_3 - T_1)$ ⇨ heat output

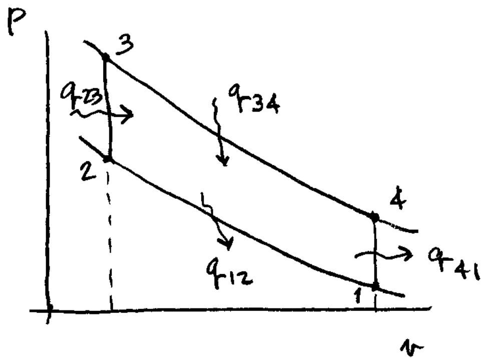
Total heat input $\underline{q_{in} = q_{23} + q_{34} = c_v(T_3 - T_1) + RT_3 \ln \frac{v_1}{v_2}}$ $\blacktriangleleft$

Thermal efficiency of the cycle, η

$$\eta = \text{thermal efficiency} = \frac{\text{Net work output}}{\text{Heat input}} = \frac{w_{net}}{q_{34} + q_{23}}$$

$$\eta = \frac{R(T_3 - T_1)\ln\frac{v_1}{v_2}}{RT_3 \ln\frac{v_1}{v_2} + c_v(T_3 - T_1)}$$ ◄

Look at the cycle in terms of the heat transfer



Note the magnitudes of q_{23} + q_{41}

$|q_{23}| = c_v(T_3 - T_1) = |q_{41}|$

Since the magnitude of the heat outpt of proces 4-1, q_{41}, is equat to the heat input of process 2-3, q_{23}, is it possible to use the heat output q_{41} to supply the required heat input q_{23}. If this is done then the only heat input will be in process 3-4, q_{34}.

Is this possible? YES! in principle. The use of an output to supply an input heat is called REGENERATION.

Since now the only external heat supplied is q_{34}, the expression for thermal efficiency becomes:

$$\eta_{REG} = \frac{w_{net}}{q_{34}} = \frac{R(T_3 - T_1)\ln\frac{v_1}{v_2}}{RT_3 \ln\frac{v_1}{v_2}} = \frac{T_3 - T_1}{T_3}$$

$$\eta_{REG} = 1 - \frac{T_1}{T_3}$$ ◄ Thermal efficiency with REGENERATION