Mayer's relation

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Julius Robert Mayer (November 25, 1814 – March 20, 1878) was a German physician, chemist and physicist and one of the founders of thermodynamics. He is best known for enunciating in 1841 one of the original statements of the conservation of energy or what is now known as one of the first versions of the first law of thermodynamics, namely that "energy can be neither created nor destroyed". In 1842, Mayer described the vital chemical process now referred to as oxidation as the primary source of energy for any living creature. His achievements were overlooked and priority for the discovery of the *mechanical equivalent of heat* was attributed to James Joule in the following year. He also proposed that plants convert light into chemical energy.

https://en.wikipedia.org/wiki/Julius_von_Mayer

The Mayer's relation is described by

$$C_P - C_V = R$$

for an ideal gas where the Boyle's law is valid, where

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P, \qquad C_V = \left(\frac{\partial Q}{\partial T}\right)_V$$

Here we present several proofs (including the general case).

(a) Method -1 (Landau)

This proof can be found in the famous textbook by Landau and Lifshitz.

The thermodynamics first law:

$$dU = TdS - PdV$$

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$\begin{aligned}
\left(\frac{\partial S}{\partial T}\right)_P &= \frac{\partial(S,P)}{\partial(T,P)} \\
&= \frac{\dfrac{\partial(S,P)}{\partial(T,V)}}{\dfrac{\partial(T,P)}{\partial(T,V)}} \\
&= \frac{1}{\left(\dfrac{\partial P}{\partial V}\right)_T}\begin{vmatrix} \left(\dfrac{\partial S}{\partial T}\right)_V & \left(\dfrac{\partial S}{\partial V}\right)_T \\ \left(\dfrac{\partial P}{\partial T}\right)_V & \left(\dfrac{\partial P}{\partial V}\right)_T \end{vmatrix} \\
&= \frac{1}{\left(\dfrac{\partial P}{\partial V}\right)_T}\left[\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial P}{\partial V}\right)_T - \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial P}{\partial T}\right)_V\right] \\
&= \left(\frac{\partial S}{\partial T}\right)_V - \frac{\left(\dfrac{\partial S}{\partial V}\right)_T\left(\dfrac{\partial P}{\partial T}\right)_V}{\left(\dfrac{\partial P}{\partial V}\right)_T}
\end{aligned}$$

Here we use the Maxwell's relation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Thus we get

$$T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V - T\frac{\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T}$$

or

$$C_P = C_V - T\frac{\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T} \qquad \text{(general case)}$$

For an ideal gas; we have the Boyle's relation

$$PV = RT$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2}, \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

Then we have

$$C_P - C_V = -T\frac{\left(\frac{R}{V}\right)^2}{\left(-\frac{RT}{V^2}\right)} = R \qquad \text{(Mayer's relation)}$$

(b) Method-2 (Kardar)

$$\begin{aligned} C_P &= \left(\frac{\partial Q}{\partial T}\right)_P \\ &= \left(\frac{dU - dW}{dT}\right)_P \\ &= \left(\frac{dU + PdV}{dT}\right)_P \\ &= \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \end{aligned} \qquad \text{(general case)}$$

For an ideal gas, U is independent of P and V, but is dependent only on T.

$$\left(\frac{\partial U}{\partial T}\right)_P = C_V\left(\frac{\partial T}{\partial T}\right)_P = C_V$$

$$P\left(\frac{\partial V}{\partial T}\right)_P = R$$

leading to the Mayer's relation.

(c) Proof given in general physics textbook (such as Halliday)

(i) Method-1

We derive a formula for the difference of C_P and C_V. If we warm a gas (n = 1 mole) slightly at constant P, we have

$$\begin{aligned} dQ &= C_P dT \\ dW &= -PdV = -RdT \\ dU &= C_V dT \end{aligned}$$

or

$$\begin{aligned} dU &= dQ + dW = C_P dT - RdT = (C_P - R)dT \\ &= C_V dT \end{aligned}$$

Then we have

$$C_P - C_V = R \qquad \text{(Mayer's relation)}$$

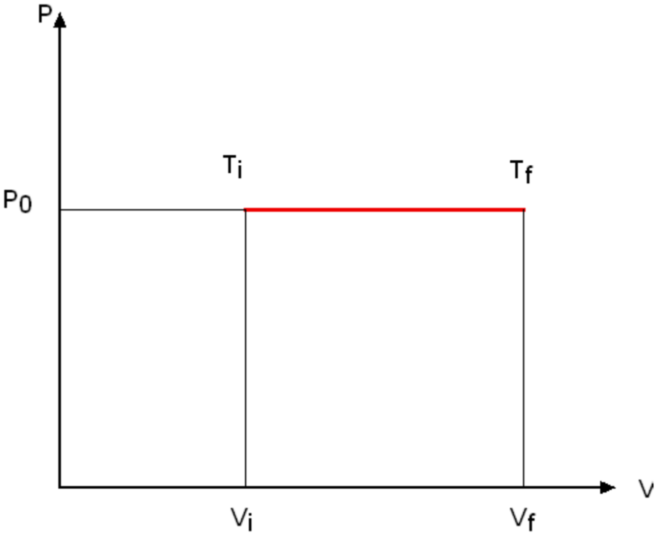
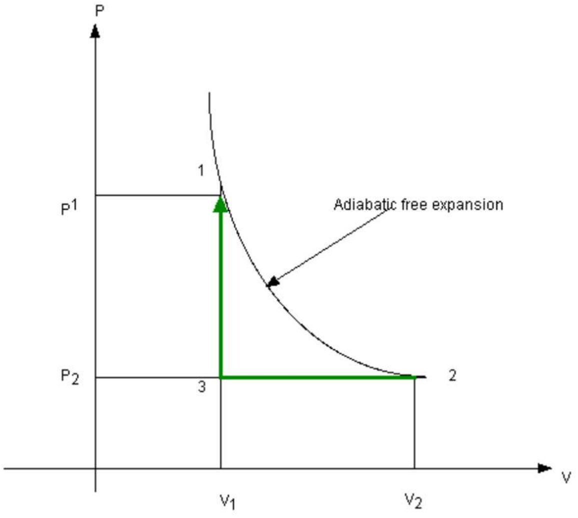


Fig. Change of volume for gas at constant P_0. $\Delta W = -\int_{V_i}^{V_f} P dV = -P_0 \Delta V = -R\Delta T$.

$\Delta U = C_V \Delta T$. $\Delta Q = C_P \Delta T$

(ii) Method-2

Using the Mayer's cycle, we show the Mayer's relation,



1: (P_1, V_1, T_1), $P_1V_1 = RT_1$

2: (P_2, V_2, T_2), $P_2V_2 = RT_2$ $(T_2 = T_1)$.

3: (P_2, V_1, T_3) $P_2V_1 = RT_3$

(1) The process 1→2 (*adiabatic free expansion*, irreversible process)

$$\Delta Q_{12} = 0, \qquad \Delta W_{12} = 0.$$

So we have

$$\Delta U_{12} = 0 \qquad (T_1 = T_2).$$

(2) The process 2→3 (pressure constant)

$$\Delta Q_{23} = C_P(T_3 - T_2)$$

$$\Delta W_{23} = -\int_{V_2}^{V_1} P_2 dV = -P_2(V_1 - V_2) = -R(T_3 - T_1)$$

$$\Delta U_{23} = \Delta Q_{23} + \Delta W_{23} = C_P(T_3 - T_2) - R(T_3 - T_1)$$

(3) The process 3→1 (volume constant)

$$\Delta Q_{31} = C_V(T_1 - T_3)$$

$$\Delta W_{31} = 0$$

$$\Delta U_{31} = \Delta Q_{31} + \Delta W_{31} = C_V(T_1 - T_3)$$

Then we have

$$\Delta U = \Delta U_{12} + \Delta U_{23} + \Delta U_{31} = C_P(T_3 - T_2) - R(T_3 - T_1) - C_V(T_3 - T_1) = 0$$

From this we have the Mayer's relation; $C_P - C_V = R$.

REFERENCES

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M. Kardar, Statistical Physics of Particles (Cambridge, 2007).

D. Halliday, R. Resnick, and J. Walker, Fundamentals of Physics, 10-th edition (Wiley, 2014).