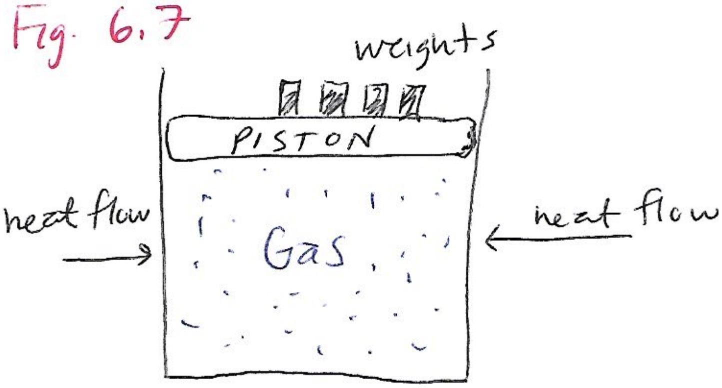
# Ideal monoatomic gas expansion

3/29/21



- Reversible isothermal expansion

KK
Fig. 6.7




The weights are removed little by little and work is done by the gas.
The work is done slowly enough that the temperature is always the same: Isothermal.

Therefore, it is always in thermodynamic equilibrium: its most probable configuration. Consider the situation in which the volume changes from $V_1$ to $V_2$.

The pressure is $pV = N\tau$. Since $N$ and $\tau$ are fixed,

$$p_1 V_1 = p_2 V_2 \quad \Rightarrow \quad p_2 = p_1 \frac{V_1}{V_2}$$

pressure is lower at larger volume

The entropy is given by the Sackur-Tetrode equation

$$\sigma = N\left[\ln(\underbrace{n_Q/n}_{n_Q V/N}) + \frac{5}{2}\right] \quad \text{with } n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$$

$$\sigma = N\left[\ln(n_Q) + \ln V - \ln N + \frac{5}{2}\right]$$

since $N$ and $\tau$ are fixed

$$\sigma_2 - \sigma_1 = N\left[\cancel{\ln(n_Q)} - \cancel{\ln(n_Q)} + \ln V_2 - \ln V_1 - \cancel{\ln N} + \cancel{\ln N} + \cancel{\tfrac{5}{2}} - \cancel{\tfrac{5}{2}}\right]$$

$$\sigma_2 - \sigma_1 = N\ln(V_2/V_1)$$

entropy is larger at larger volume

KK Eq. 6.56

The work done ~~against~~ the piston is (by the gas)

$$W = \int_{V_1}^{V_2} p\,dV = \int_{V_1}^{V_2} (N\tau/V)\,dV = N\tau \int_{V_1}^{V_2} \frac{dV}{V}$$ since $N$ and $\tau$ are constant

$$W = N\tau \ln V \Big|_{V_1}^{V_2} = N\tau \ln(V_2/V_1)$$ KK Eq. 6.57

Notice also $W = \tau(\sigma_2 - \sigma_1)$

The work done by the gas is $-W$.

The internal energy of the ideal gas is $U = \frac{3}{2} N\tau$.
Since both $N$ and $\tau$ are fixed, the internal energy remains the same. From the thermodynamic identity,

$$\tau\, d\sigma = dU + p\,dV$$ but $dU = 0$ in isothermal case

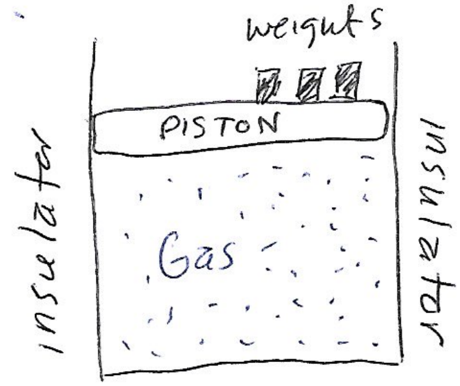
$$\underbrace{\int \tau\, d\sigma}_{\text{heat flow}} = \underbrace{\int p\,dV}_{\text{work done}} \Rightarrow Q = -W \quad \text{or} \quad Q + W = 0$$

(1st law of thermodynamics)

heat flow can increase the internal energy of a gas, but work done by the gas decreases the internal energy. If the temperature remains constant, the work done by the gas comes ~~[illegible]~~ from the heat flow.

## Reversible isentropic expansion (adiabatic)






The weights are removed little by little and work is done by the gas. The work is done slowly enough that the entropy is always the same, so isentropic. The term "adiabatic" means no heat transfer, but isentropic is more precise. Consider the situation in which the volume changes from $V_2$ to $V_1$.

The entropy is given by the Sackur - Tetrode equation

$$\sigma = N\left[\ln(n_Q) + \ln V - \ln N + \frac{5}{2}\right]$$

$$\sigma = N\left[\ln \tau^{3/2} + \ln V + \ln\left(\frac{m}{2\pi\hbar^2}\right)^{3/2} - \ln N + \frac{5}{2}\right]$$

KK Eq. 6.61

$$\sigma = N\left[\ln \tau^{3/2} + \ln V + \text{constant}\right]$$

$$\sigma_2 - \sigma_1 = \cancel{N}\left[\ln \tau_2^{3/2} - \ln \tau_1^{3/2} + \ln V_2 - \ln V_1 + \cancel{\text{const.}} - \cancel{\text{const.}}\right] = 0$$

$$\ln\left(\frac{\tau_2}{\tau_1}\right)^{3/2} = -\ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{V_1}{V_2}\right) \Rightarrow \tau_1^{3/2} V_1 = \tau_2^{3/2} V_2$$

KK Eq. 6.63

$$\boxed{\text{temperature is lower at larger volume}}$$

Since $pV = N\tau \Rightarrow p = \frac{N\tau}{V}$ and $\frac{\tau_1}{\tau_2} = \left(\frac{V_2}{V_1}\right)^{2/3}$

$$\frac{p_2}{p_1} = \frac{\frac{N\tau_2}{V_2}}{\frac{N\tau_1}{V_1}} = \frac{V_1}{V_2}\cdot\frac{\tau_2}{\tau_1} = \frac{V_1}{V_2}\left(\frac{V_1}{V_2}\right)^{2/3} = \frac{V_1^{5/3}}{V_2^{5/3}}$$

so $p_1 V_1^{5/3} = p_2 V_2^{5/3}$ KK Eq. 6.65 $\quad p_2 = p_1 \left(\frac{V_1}{V_2}\right)^{5/3}$

Since $pV = N\tau$, $V = \frac{N\tau}{p}$

$\boxed{\text{pressure is lower at larger volume}}$

$$\tau_1^{3/2} \frac{\cancel{N}\tau_1}{p_1} = \tau_2^{3/2} \frac{\tau_2 \cancel{N}}{p_2} \Rightarrow \frac{\tau_1^{5/2}}{p_1} = \frac{\tau_2^{5/2}}{p_2}$$ KK Eq. 6.64

The work done <u>against</u> the piston by the gas is

$$W = \int_{V_1}^{V_2} p\,dV$$

Since $p_1 V_1^{5/3} = p_2 V_2^{5/3} \Rightarrow pV^{5/3} = \text{constant} = pVV^{2/3}$

$$d(pV^{5/3}) = d(\underbrace{p}_{u}\,\underbrace{V}_{v}\,\underbrace{V^{2/3}}_{w}) = 0$$ product rule for three terms

$$pV\,dV^{2/3} + V V^{2/3}\,dp + V^{2/3} p\,dV = 0$$

product rule for two terms

$$V^{2/3}\left[V\,dp + p\,dV\right] + pV\,dV^{2/3} = 0$$

$\frac{dx^n}{dx} = nx^{n-1}$

$\Rightarrow dx^n = nx^{n-1}\,dx$

$$V^{2/3}\,d(pV) + pV\left(\tfrac{2}{3}\right)V^{-1/3}\,dV = 0$$

$$V^{2/3}\,d(pV) + \left(\tfrac{2}{3}\right)p\cancel{V}\frac{V^{2/3}}{\cancel{V}}\,dV = 0$$

$$\frac{2}{3}p\cancel{V^{2/3}}\,dV = -\cancel{V^{2/3}}\,d(pV)$$

$$p\,dV = -\frac{3}{2}\,d(pV)$$

Since $pV = N\tau$, $p\,dV = -\frac{3}{2}\,d(N\tau) = -\frac{3}{2}N\,d\tau$

$$W = \int_{V_1}^{V_2} p\,dV = -\frac{3}{2}N\int_{\tau_1}^{\tau_2} d\tau = -\frac{3}{2}N(\tau_2 - \tau_1)$$

Remember that $U = \frac{3}{2} N \tau$, so

$$U_2 - U_1 = \frac{3}{2} N (\tau_2 - \tau_1)$$ KK Eq. 6.71

$$W = -\Delta U$$

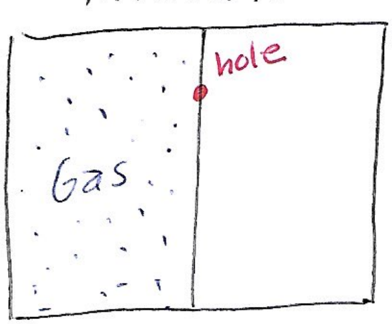
From the thermodynamic identity $\tau d\sigma = dU + pdV$

since $d\sigma = 0$ (there is no heat flow) $pdV = W = -dU$

(1st law of thermodynamics)

work done by the gas decreases its internal energy.

- Irreversible expansion into a vacuum




A hole is opened in the partition to permit expansion. The expansion ~~is~~ happens rapidly and, since there was nothing to expand against, <u>no work</u> is done. Because the expansion is rapid, the system is only in thermodynamic equilibrium before expansion and after the gas fills both chambers. Since the expansion is rapid and the system is isolated, no heat flows.

No work is done and no heat flows, so $dU = 0$ and $U_2 = U_1 = \frac{3}{2} N \tau$. The temperature of the gas is the same before and after.

The change in entropy is $\sigma = N\left[\ln\left(\frac{n_Q V}{N}\right) + \frac{5}{2}\right]$

$$\sigma_2 - \sigma_1 = N \ln(V_2/V_1)$$ KK Eq. 6.73

The thermodynamic equation does not hold because the system was not in thermodynamic equil.

In summary,



| Expansion type | $\Delta U$ | $\Delta \sigma$ | $W$ | $Q$ |
|---|---|---|---|---|
| Reversible isothermal expansion | $0$ | $N \ln\left(\frac{V_2}{V_1}\right)$ | $-N\tau \ln\left(\frac{V_2}{V_1}\right)$ | $N\tau \ln\left(\frac{V_2}{V_1}\right)$ |
| Reversible isentropic expansion | $-\frac{3}{2}N\tau_1\left[1-\left(\frac{V_1}{V_2}\right)^{2/3}\right]$ | $0$ | $-\frac{3}{2}N\tau_1\left[1-\left(\frac{V_1}{V_2}\right)^{2/3}\right]$ | $0$ |
| Irreversible expansion into vacuum | $0$ | $N \ln\left(\frac{V_2}{V_1}\right)$ | $0$ | $0$ |