# Statistical Molecular Thermodynamics

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Video 4.3

Ideal Monatomic Gas: Properties

# Monatomic Ideal Gas $Q$

We have derived that for a *monatomic ideal gas*:

$$Q(N,V,T) = \frac{\left[q_{\text{trans}}(V,T)\, q_{\text{elec}}(T)\right]^{N}}{N!}$$

where $$q_{\text{trans}}(V,T) = \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V$$

$$q_{\text{elec}}(T) \approx g_1 + g_2 e^{-\beta\varepsilon_2}$$

# Monatomic Ideal Gas Internal Energy $U$

indistinguishable, non-interacting molecules/atoms

$$Q(N,V,T) = \frac{q(V,T)^N}{N!}$$

$$q(V,T) = q_{\text{trans}}(V,T)\, q_{\text{elec}}(T)$$

monatomic gas

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = N k_B T^2 \left(\frac{\partial \ln q}{\partial T}\right)_V = N k_B T^2 \left[\frac{\partial \ln\left(q_{\text{trans}}\, q_{\text{elec}}\right)}{\partial T}\right]_V$$

$$U = N k_B T^2 \left\{\frac{\partial}{\partial T} \ln\left[\underbrace{\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V}_{q_{\text{trans}}}\ \underbrace{\left(g_1 + g_2 e^{-\beta\varepsilon_2} + \cdots\right)}_{q_{\text{elec}}}\right]\right\}_V = \frac{3}{2} N k_B T + \cdots \quad ?$$

# Monatomic Ideal Gas Internal Energy $U$

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$$U = N k_B T^2 \left\{\frac{\partial}{\partial T} \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V \left(g_1 + g_2 e^{-\beta\varepsilon_2} + \cdots\right)\right]\right\}_V = \frac{3}{2} N k_B T + \frac{N g_2 \varepsilon_2 e^{-\beta\varepsilon_2}}{q_{\text{elec}}} + \cdots$$

$q_{\text{trans}}$ $q_{\text{elec}}$

$q_{\text{elec}}$ contribution typically small

$$U \approx \frac{3}{2} N k_B T$$

Dominated by translational contribution. Fraction in excited electronic states usually very small at “low” temperatures

# Monatomic Ideal Gas Internal Energy $U$

$$U = Nk_BT^2\left\{\frac{\partial}{\partial T}\ln\left[\underbrace{\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}V}_{q_{trans}}\underbrace{\left(g_1 + g_2e^{-\beta\varepsilon_2} + \cdots\right)}_{q_{elec}}\right]\right\}_V = \frac{3}{2}Nk_BT + \frac{Ng_2\varepsilon_2e^{-\beta\varepsilon_2}}{q_{elec}} + \cdots$$

$q_{elec}$ contribution typically small

$$U \approx \frac{3}{2}Nk_BT$$

for $N = N_A$, $T = 298.15$ K, energy in kJ

$q_{elec}$=4.142 (F)

| | Li<br>$\varepsilon_2 = 14903.66\ \text{cm}^{-1}$<br>$g_2 = 2$ | F<br>$\varepsilon_2 = 404.0\ \text{cm}^{-1}$<br>$g_2 = 2$ |
|---|---|---|
| $\frac{3}{2}Nk_BT$ | 3.719 | 3.719 |
| $\frac{Ng_2\varepsilon_2e^{-\beta\varepsilon_2}}{q_{elec}}$ | 2.081 x $10^{-26}$ | 0.332 |

# Monatomic Ideal Gas Heat Capacity $C_V$

$$U = \frac{3}{2}Nk_BT + \frac{Ng_2\varepsilon_2 e^{-\varepsilon_2/k_BT}}{q_{elec}} + \cdots$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \left[\frac{\partial\left(\frac{3}{2}Nk_BT + Ng_2\varepsilon_2 e^{-\varepsilon_2/k_BT}/q_{elec} + \cdots\right)}{\partial T}\right]_{N,V} = \frac{3}{2}Nk_B + \frac{Ng_2\varepsilon_2^2}{k_BT^2 q_{elec}}e^{-\varepsilon_2/k_BT} + \cdots$$

| | Li<br>$\varepsilon_2 = 14903.66\ \text{cm}^{-1}$<br>$g_2 = 2$ | F<br>$\varepsilon_2 = 404.0\ \text{cm}^{-1}$<br>$g_2 = 2$ |
|---|---|---|
| $\frac{3}{2}Nk_B$ | 12.47 | 12.47 |
| $\frac{Ng_2\varepsilon_2^2}{k_BT^2 q_{elec}}e^{-\varepsilon_2/k_BT} + \cdots$ | 5.020 x $10^{-27}$ | 2.172 |

for $N = N_A$,
$T = 298.15$ K,
$C_V$ in J•K$^{-1}$

# Monatomic Ideal Gas Pressure $P$

indistinguishable, non-interacting molecules/atoms

$$Q(N,V,T) = \frac{q(V,T)^N}{N!}$$

$$q(V,T) = q_{\text{trans}}(V,T)\, q_{\text{elec}}(T)$$

monatomic gas

$$P = k_B T\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = Nk_B T\left(\frac{\partial \ln q}{\partial V}\right)_T = Nk_B T\left[\frac{\partial \ln\left(q_{\text{trans}}\, q_{\text{elec}}\right)}{\partial V}\right]_T$$

$$P = Nk_B T\left\{\frac{\partial}{\partial V}\ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V\left(g_1 + g_2 e^{-\beta\varepsilon_2} + \cdots\right)\right]\right\}_T = Nk_B T\left(\frac{\partial}{\partial V}\ln V\right)_T = \frac{Nk_B T}{V}$$

the only function of $V$

$$P = \frac{Nk_B T}{V}$$

Ideal Gas Law ($PV=nRT$)

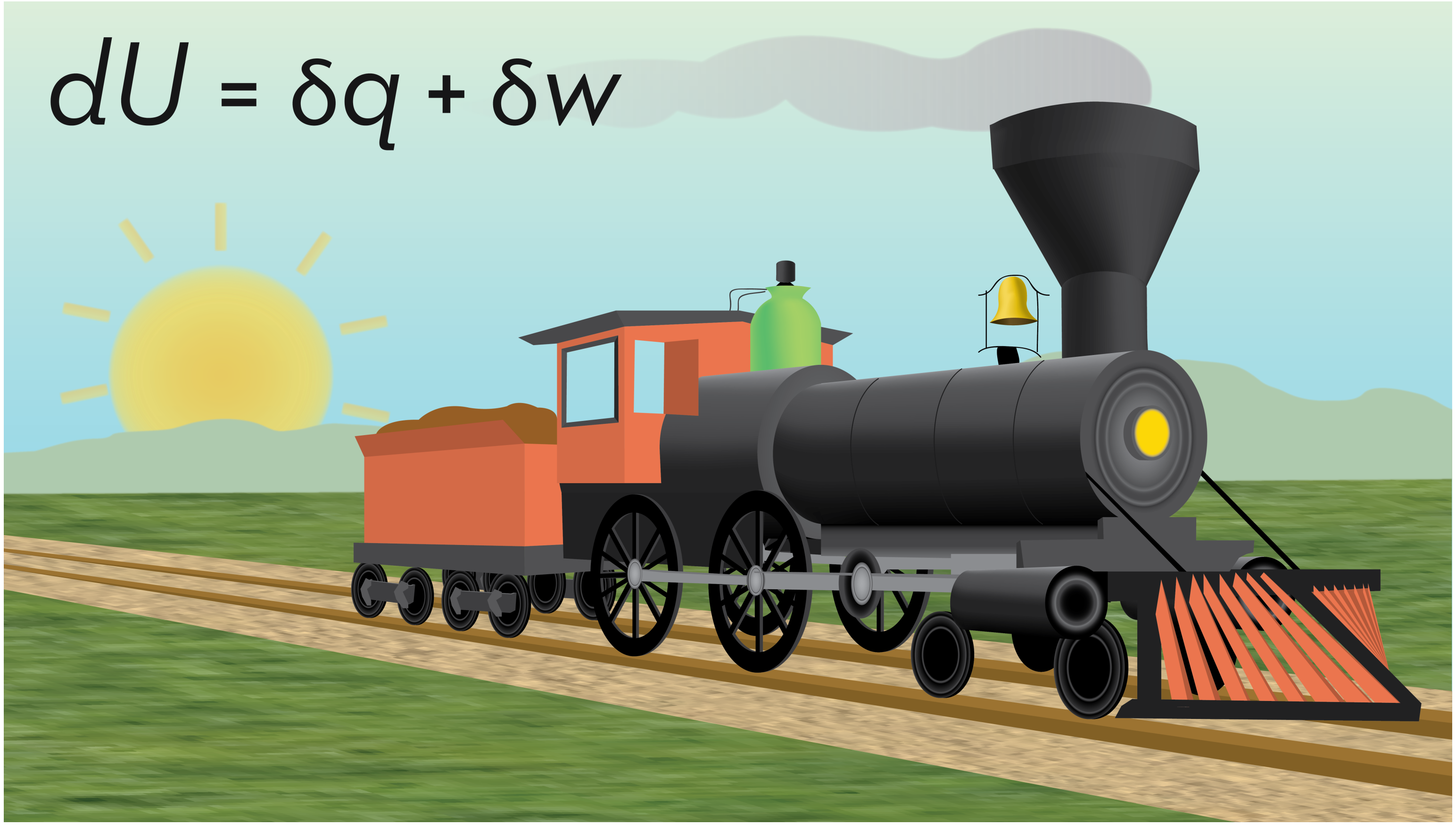
# Summary: Monatomic Ideal Gas

**Partition function:**

$$Q(N,V,T) = \frac{\left(q_{\text{trans}}(V,T)\,q_{\text{elec}}(T)\right)^N}{N!}$$

$$q_{\text{trans}}(V,T) = \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V \qquad q_{\text{elec}}(T) \approx g_1 + g_2 e^{-\beta\varepsilon_2}$$

| | | (molar) |
|---|---|---|
| • **Energy** | $U = \frac{3}{2} N k_{\text{B}} T$ | $\overline{U} = \frac{3}{2} RT$ |
| • **Heat Capacity** | $C_V = \frac{3}{2} N k_{\text{B}}$ | $\overline{C}_V = \frac{3}{2} R$ |
| • **Pressure** | $P = \frac{N k_{\text{B}} T}{V}$ | $P = \frac{RT}{\overline{V}}$ |




*Next: Ideal Diatomic Gas: Part 1*