Formula sheet for Thermodynamics

Physical constants

k_B	1.381×10^{-23} J/K,
N_A	6.022×10^{23},
R	8.315 J/mol·K,
e	1.602×10^{-19} C.

1 General

- The ideal gas law: $PV = Nk_BT$, $PV = nRT$.
- Equipartition: $U_{\text{thermal}} = \frac{f}{2}Nk_BT$.
- First law of thermodynamics: $dU = W + Q$.
- Work: $W = -\int_{V_i}^{V_f} P(V)dV$, (quasistatic).
- Adiabatic process: $PV^\gamma = \text{const}$, $\gamma = \frac{f+2}{f}$.
- Heat capacity:

$$C = \frac{Q}{\Delta T}, \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V, \quad C_P = \left(\frac{\partial H}{\partial T}\right)_P.$$

- Latent heat: $L = Q/m$.
- Thermal conductivity: $\frac{Q}{\Delta t} = -\kappa_t A \frac{dT}{dx}$.

2 The second law

- Multiplicity of a two-state paramagnet: $\Omega(N, N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!}$.
- Stirling's approximation: $\ln N! \approx N \ln N - N$.
- Entropy from multiplicity: $S = k_B \ln \Omega$.
- The Sackeur-Tetrode formula:

$$S = Nk_B \left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right]$$

3 Interactions and implications

- Definition of temperature: $T = \left(\frac{\partial S}{\partial U}\right)^{-1}$.
- The thermodynamic identity: $dU = TdS - PdV + \mu dN$.
- Entropy and heat: $S = Q/T$.

4 Engines and refrigerators

- Heat engine: $Q_h = Q_c + W_e$.
  In the context of heat engines we let W_e be positive when energy is leaving the system. This is thus an exception from the ordinary sign convention.
- Efficiency: $\eta = \text{benefit}/\text{cost} = W_e/Q_h$.
- Carnot efficiency: $\eta = 1 - T_c/T_h$.

5 Free energy and chemical thermodynamics

- Enthalpy: $H = U + PV$ and $dH = TdS + VdP + \mu dN$.
- Helmholtz free energy: $F = U - TS$ and $dF = -SdT - PdV + \mu dN$.
- Gibbs free energy: $G = U + PV - TS$ and $dG = -SdT + VdP + \mu dN$.
- Chemical potential: $\mu = G/N$.
- $\Delta G \leq W_{\text{other}}$ (at constant T and P).
- The Clausius-Clapeyron relation

$$\frac{dP}{dT} = \frac{L}{T\Delta V}.$$