h = 1.054×10^{-34} \text{ J-s} \quad k_B = 1.38×10^{-23} \text{ J/K} \quad N_A = 6.02×10^{23} \quad m_e = 9.11×10^{-31} \text{ kg}

m_p = 1.66×10^{-27} \text{ kg} \quad 1 \text{ Å} = 10^{-10} \text{ m} \quad 1 \text{ eV} = 1.602×10^{-19} \text{ J} \quad 1 \text{ amu} = 1.66×10^{-27} \text{ kg}

T = 300 \text{ K} \text{ corresponds to } \tau = k_B \times 300 \text{ K} = 25.8×10^{-3} \text{ eV.}

1. a) Write down the Fermi-Dirac distribution function, \( f(\varepsilon, \tau, \mu) \), for a system with many (\( N \gg 1 \)) identical fermions. Sketch \( f(\varepsilon, \tau, \mu) \) vs. energy, \( \varepsilon \), for \( \tau \approx 0 \) and \( \tau \approx \varepsilon_F/10 \). Assume the energy of the lowest energy state is \( \varepsilon = 0 \). Be sure to label axes and include scales.

\[ f(\varepsilon, \tau, \mu) = \]

See KK pages 154 and 156.

b) Write down an integral expression for the energy of a gas of fermions as a function of temperature. The integrand should involve the density of states and fermi function. Sketch the integrand vs. energy for a 3-dimensional system.

\[ U(\tau) = U(0) + \]

See KK page 188.
c) Name two fermions and two bosons.

Fermions: electrons, protons, neutrons, helium-3 atoms

Bosons: photons, phonons, helium-4 atoms, gravitons, H atoms.

2. a) Sketch the p-V diagram for a Carnot cycle heat engine. Label each segment of the cycle, e.g., adiabat or isochor or isotherm or isobar.

See KK page 239.

b) What are the constraints that thermodynamics puts on each cycle of a heat engine?

1. Conservation of energy says that the net work output equals the heat extracted from the hot reservoirs minus the heat delivered to the cold reservoir.

2. Maximization of entropy says that the reduction in entropy of the hot reservoir, caused by removal of heat from it, must be less than or equal to the increase in entropy of the cold reservoir, caused by addition of heat to it: \( \frac{Q_h}{\tau_h} \leq \frac{Q_c}{\tau_c} \).
3. a) The enthalpy change in converting $\frac{1}{2}$ mole of O$_2$ to 1 mole of atomic oxygen, O, at 298 K and atmospheric pressure is 249 kJ. Neglecting kinetic energies and work done during the reaction, calculate the bonding energy of one O$_2$ molecule. Give your answer in electron volts.

**O-O Bond energy is:** $\epsilon_B$ eV.

$$\epsilon_B = \frac{249 \text{ kJ}}{0.5 \text{ mole of O-O bonds}} = 8.3 \times 10^{-19} \text{ J} = 5.16 \text{ eV}.$$ 

b) Assuming that rotations are classical and vibrations are frozen out, calculate the net change in kinetic energy in the formation of 1 mole of O.

**$\Delta$KE. =** kJ.

Kinetic energy of 1 mole of O is: $N_A \times 1.5\tau$.

Kinetic energy of $\frac{1}{2}$ mole of O$_2$ is: $\frac{1}{2} N_A \times 2.5\tau$.

Net change is: $N_A\tau \times (1.5 - 1.25) = N_A\tau/4 = 567 \text{ J}.$

c) Calculate the net work done by the system on the thermal reservoir during the reaction.

**Work =** kJ.

When the number of molecules goes from $\frac{1}{2}$ mole to 1 mole, the volume increases from $\frac{1}{2} \times 24.5$ liters to 24.5 liters. Thus, $\Delta V = 12.25 \text{ liter}$.

Net work = $p\Delta V = 1 \text{ atm} \times 12.25 \text{ liter} = 10^5 \text{ N/m}^2 \times 12.1 \times 10^{-3} \text{ m}^3 = 1.24 \text{ kJ}$. 
3. a) Sketch the phase (p-T) diagram of a typical single-component system, e.g., carbon dioxide CO₂. Label the different phase regions, and label important points.

![Phase diagram of carbon dioxide CO₂](image)

b) Treat solid CO₂ as having a free energy dominated by a bonding energy of $\varepsilon_B = 0.4 \text{ eV}$ per molecule. (Neglect phonons.) Treat gaseous CO₂ as a diatomic ideal gas with a moment of inertia, $I = 2 \times 16 \text{amu} \times 1 \text{ Å}^2$. Treat rotations as classical, but neglect vibrations. Derive an expression for the equilibrium vapor pressure of solid CO₂. Estimate the equilibrium vapor pressure of CO₂ at 200 K.

$$P_{\text{eq}}(\tau) = (\ln \tau^2 / \hbar^2) \exp(-\varepsilon_B / \tau)$$

$$P_{\text{eq}}(200\text{K}) =$$

Equilibrium means $\mu_{\text{sol}} = \mu_{\text{gas}}$. We get $\mu$’s from: $\mu \equiv \partial F / \partial N|_{T,V}$.

$$\mu_{\text{solid}} = \partial F_{\text{solid}} / \partial N|_{T,V} = -\varepsilon_B; \quad \mu_{\text{gas}} = \tau \log(n/n_0) - \tau \log(\tau I / \hbar^2) = \tau \log(n \hbar^2 / \ln \tau^2).$$

The ideal gas law allows us to express the chemical potential of the gas in terms of pressure, $p$, by replacing $n$ with $p/\tau$. Thus, equilibrium requires:

$$-\varepsilon_B / \tau = \log(p \hbar^2 / \ln \tau^2).$$

Exponentiating and rearranging leads to:

$$p = (\ln \tau^2 / \hbar^2) \exp(-\varepsilon_B / \tau).$$
4. Consider a single-component van der Waals fluid in contact with P and \( \tau \) reservoirs. Neglect vibrational and rotational degrees of freedom.

a) Write down energy \( U \) and entropy \( \sigma \) and Helmholtz free energy \( F \) as functions of \( \tau, V, \) and \( N \).

\[
U(\tau,V,N) = 1.5N\tau - AN^2/2V.
\]

\[
\sigma(\tau,V,N) = N\log[n_Q(V-Nb)/N] + 2.5N
\]

\[
F(\tau,V,N) = -N\tau - AN^2/2V - N\tau \log[n_Q(V-Nb)/N].
\]

b) Derive pressure \( p(\tau,V,N) \) for a homogeneous van der Waals fluid. Explain the microscopic origins of differences from the ideal gas equation of state.

\[
p(\tau,V,N) = N\tau/(V-Nb) - AN^2/2V^2
\]

Use \( p = -\partial F(\tau,V,N)/\partial V|_{\tau,N} \) to get: \( p = N\tau/(V-Nb) - AN^2/2V^2 \).

Short-range repulsion between particles increases the pressure that the gas exerts on the walls of its container, as described by the replacement of the ideal gas term, \( N\tau/V \), with \( N\tau/(V-Nb) \) in the van der Waals equation of state.

Long-range attraction between particles lessens the pressure that the gas exerts on the walls of its container, as described by the new negative term, \(-AN^2/V^2\), that appears for the van der Waals gas, but not for the ideal gas.
c) Sketch three isotherms (p vs. V) for a van der Waals fluid: one at the critical temperature, $\tau_c$, and others at higher and lower temperatures.

See KK p. 290, Fig. 10.10, for numerically calculated curves.

d) Sketch an isotherm at a temperature below critical for a van der Waals fluid. Show where the liquid-gas phase transition occurs.

See KK p. 290, Fig. 10.10, curve for $\tau = 0.95\tau_c$.

e) What properties must be the same for the liquid and the gas when they are in equilibrium?

Same pressure, temperature, and chemical potential.