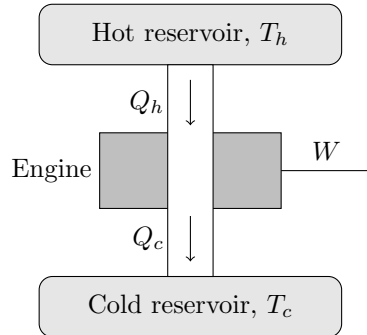


## 1 Lecture 14 (April 21st)

## 2 Lecture 15 (April 30th)

### Chapter 4.1 Heat Engines

**Definition.** (Heat engine and its efficiency) A heat engine is any device that absorbs heat and converts part of that energy into work.



Take  $W$ ,  $Q_h$ , and  $Q_c$  to be greater than zero. The efficiency of an engine is defined as the work done over the total amount of heat provided,

$$\varepsilon = \frac{\text{benefit}}{\text{cost}} = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

Meanwhile, the second law of thermodynamics states that the total entropy of the engine plus its surroundings can increase but not decrease. Notice how after 1 cycle,

$$\Delta S_{tot} = \frac{Q_c}{T_c} - \frac{Q_h}{T_h} \geq 0$$

and

$$\varepsilon = 1 - \frac{Q_c}{Q_h} \leq 1 - \frac{T_c}{T_h}$$

### Chapter 4.2 Refrigerator

**Definition.** A refrigerator is a heat engine operated in reverse, where work is put in the engine and not pulled out of it. Then, heat is pushed into the Kitchen. The relevant metric is coefficient of performance (COP),

$$\text{COP} = \frac{\text{benefit}}{\text{cost}} = \frac{Q_c}{W} = \frac{1}{Q_h/Q_c - 1} \leq \frac{1}{T_h/T_c - 1}$$

### 3 Lecture 16 (May 7th)

**Remark.** (Liquefaction of gases) If you want to make something really cold, you normally don't just stick it into a refrigerator – instead you put it on dry ice, immerse it in liquid nitrogen, or even liquid helium. These gases are liquefied in the first place using a throttling process.

## Chapter 5 Free Energy and Chemical Thermodynamics

### Chapter 5.1 Free Energy and Available Work

**Definition.** (Free energies) There is Helmholtz free energy  $F$  and Gibbs free energy  $G$ .

$$\begin{cases} F = U - TS \\ G = H - TS = U + PV - TS \end{cases}$$

At constant  $T$ , we can think of these energies as quantities that are minimised as  $\Delta V = 0$  and  $\Delta P = 0$  respectively.

$$\begin{array}{c} \xrightarrow{-TS} \\ \begin{array}{|c|c|} \hline U & F \\ \hline H & G \\ \hline \end{array} \\ \downarrow +PV \end{array}$$

*Proof.* At constant  $T$ ,

$$\Delta F = \Delta U - T\Delta S = Q + W - T\Delta S$$

Since  $T\Delta S \geq Q$ , we have  $\Delta F \leq W$ . On the other hand,

$$\Delta G = \Delta U - T\Delta S + P\Delta V = Q + W - T\Delta S + P\Delta V$$

Since  $T\Delta S \geq Q$ , we have  $\Delta G \leq W$ . Therefore, in each case, we see the difference in free energies to be less than the work done by an external system.  $\square$

## 4 Lecture 17 (May 12th)

**Theorem.** (Pressure, chemical potential, and entropy in terms of  $F$  and  $G$ ) Notice that from the thermodynamic identity  $dU = T dS - P dV + \mu dN$

$$\begin{aligned} F &= U - TS \\ dF &= dU - T dS - S dT \\ &= (T dS - P dV + \mu dN) - T dS - S dT \\ &= -P dV + \mu dN - S dT \end{aligned}$$

as  $F = F(T, V, N)$ . We conclude that

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \quad S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

By a similar argument, we also have  $G = G(T, P, N)$  and

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N} \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

## Chapter 5.2 Free Energy as a Force Toward Equilibrium

## 5 Lecture 18 (May 14th)

### Chapter 5.3 Phase transformations of Pure Substances

**Definition.** A phase transform is a discontinuous change in the properties of a substance as its environment is changed only infinitesimally.

## 6 Lecture 19 (May 19th)

### Chapter 5.4 Phase transformation of mixture

## 7 Lecture 20 (May 21st)

## 8 Lecture 22 (May 26th)

## 9 Lecture 23 (May 28th)

### Chapter 6.1 The Boltzmann factor

**Definition.** (Boltzmann factor) The Boltzmann factor is defined as the increase of the number of states as a system gains a small amount of energy  $\varepsilon$  from the ground state.

$$\frac{\Omega(E_T - \varepsilon)}{\Omega(E_T)} = \frac{\exp(S(E_T - \varepsilon)/k)}{\exp(S(E_T)/k)}$$

**Definition.** (Partition function) The partition function is defined as the sum of all Boltzmann factors

$$Z = \sum_S \exp\left(-\frac{E(s)}{kt}\right)$$

Since the probability to be at the state  $S$  is proportional to the Boltzmann factor,

$$P(S) \propto \exp\left(-\frac{E(s)}{kt}\right)$$

and

$$P(S) = \frac{1}{Z} \exp\left(-\frac{E(S)}{kt}\right) = \frac{1}{Z} \exp(-\beta E(S))$$

where  $\beta = 1/kT$ .

## Chapter 6.2 Average values

**Definition.** (Energy average value) The energy average value is defined as the weighted average of the energy of a system.

$$\bar{E} = \sum_S E(S) \cdot P(S) = \frac{1}{Z} \sum_S E(S) \exp\left(-\frac{E(S)}{kT}\right)$$

Extending this argument, for any quantity  $X(S)$ ,

$$\bar{X} = \frac{1}{Z} \sum_S X(S) \exp\left(-\frac{E(S)}{kt}\right)$$

**Definition.** Previously, we looked at *micro-canonical ensembles*. However, now on, we look at *canonical ensembles*.

**Theorem.** The average energy is related with the partition function by

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z$$

or, equivalently,

$$\bar{E} = -\frac{\partial T}{\partial \beta} \frac{\partial}{\partial T} \ln Z = kT^2 \cdot \frac{\partial}{\partial T} \ln Z$$

*Proof.*

$$Z = \sum_S e^{-\beta E(S)}$$

and

$$\frac{\partial Z}{\partial \beta} = \sum_S (-E(S)) e^{-\beta E(S)}$$

leading to

$$\bar{E} = \frac{1}{Z} \sum_S E(S) e^{-\beta E(S)} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

□

**Example.** (Paramagnetism) Let's apply the Boltzmann factor to the ideal two-state paramagnet. The partition function is given by

$$Z = \sum_S e^{-\beta E(S)} = e^{\beta \mu B} + e^{-\beta \mu B} = 2 \cosh(\beta \mu B)$$

The average energy, on the other hand, is

$$\bar{E} = \frac{1}{Z} \sum_S E(S) e^{-\beta E(S)} = \frac{-\mu B [e^{\beta \mu B} - e^{-\beta \mu B}]}{2 \cosh(\beta \mu B)} = -\mu B \tanh(\beta \mu B)$$

For a collection of  $N$  dipoles,  $U = N\bar{E} = -N\mu B \tanh(\beta \mu B)$ .

**Example.** (Equipartition theorem) Classically, rotation of diatomic molecules are given as

$$E = \frac{L_x^2}{2I_x} + \frac{L_y^2}{2I_y}$$

while in a quantum mechanical setting,

$$E(j) = j(j+1)\epsilon$$

with degeneracy  $2j+1$ . The partition function is given as

$$Z = \sum_{j=0}^{\infty} (2j+1) \exp\left(-\frac{j(j+1)\epsilon}{kT}\right)$$

For  $kT \gg \epsilon$ , the number of terms that contribute significantly to the partition function will be quite large. So

$$Z \approx \int_0^{\infty} (2j+1) e^{-j(j+1)\epsilon/kT} dj = \int_0^{\infty} \frac{kT}{\epsilon} e^{-x} dx = \frac{kT}{\epsilon} \left[ -e^{-x} \right]_0^{\infty} = kT/\epsilon$$

Now using  $\bar{E} = -\partial \ln Z / \partial \beta$ ,

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln \left( \frac{1}{\beta \varepsilon} \right) = \frac{1}{\beta} = kT$$

This is just the prediction of the equipartition theorem!

$$\bar{E} = \frac{f}{2} \cdot kT$$

**Remark.** For diatomic molecules made of distinguishable atoms (for example, carbon dioxide), previous results are correct. However, for molecules made of identical atoms (for example, nitrogen or oxygen dioxide), indistinguishability should be considered.

### Chapter 6.3 The equipartition theorem

**Recall.** The equipartition theorem stated that for systems whose energy is in the form of quadratic degrees of freedom,

$$E = \sum_i^f c_i q_i^2 \quad \implies \quad \bar{E} = \frac{f}{2} \cdot kT$$

## 10 Lecture 24 (June 2nd)

### Chapter 6.4 The Maxwell speed distribution

**Definition.** The Maxwell speed distribution is the distribution of the speed of a gas molecule with temperature  $T$ . The area  $D(v) \cdot dv$  is the probability for the gas molecule to be between  $v$  and  $v + dv$ .

$$\mathcal{D}(v) = \left( \frac{m}{2\pi kT} \right)^{3/2} \cdot 4\pi v^2 \cdot \exp \left( -\frac{mv^2}{2kT} \right)$$

*Proof.* As the distribution should be proportional to the probability of a molecule to have a velocity of  $\mathbf{v}$  times the number of vectors  $\mathbf{v}$  corresponding to the speed  $v$ , we have

$$\mathcal{D}(v) = c \cdot 4\pi v^2 \cdot \exp \left( -\frac{mv^2}{2kT} \right)$$

since the total probability should be 1, we find the constant to be

$$c = \left( \frac{m}{2\pi kT} \right)^{3/2}$$

The Maxwell-Boltzmann distribution is therefore given as

$$\mathcal{D}(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} \cdot 4\pi v^2 \cdot \exp\left(-\frac{mv^2}{2kT}\right)$$

□

**Corollary.** The most probable speed is given as

$$v_{max} = \sqrt{\frac{2kT}{m}}$$

The average speed is given as

$$\bar{v} = \sqrt{\frac{8kT}{m\pi}}$$

The root-mean-square speed is given as

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$