Chapter 7 — Applications

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Part I
Thermal Machines

Thermal machines are devices that convert thermal energy into mechanical work (engines) or, conversely, use work to transfer heat from a cold source to a hot source (refrigerators, heat pumps).

1 Thermal Machines

1.1 Ideal Thermal Machines

1.1.1 Review: Carnot Cycle

The Carnot cycle is the reference theoretical reversible cycle. It operates between two thermostats at temperatures T_c (hot source) and T_f (cold source, $T_f < T_c$) and consists of four reversible transformations:

1. Isothermal expansion at T_c (absorption of $Q_c > 0$).
2. Reversible adiabatic expansion ($T_c \to T_f$).
3. Isothermal compression at T_f (rejection of $Q_f < 0$).
4. Reversible adiabatic compression ($T_f \to T_c$).

The efficiency of a Carnot engine is:

$$\eta_{\text{Carnot}} = 1 - \frac{T_f}{T_c} \qquad (1.1) \tag{1}$$

Carnot's Theorem

No thermal machine operating between two given sources can have an efficiency greater than that of a Carnot machine operating between the same sources.

1.1.2 Stirling Cycle

The Stirling cycle is an ideal regenerative cycle consisting of:

1. Isothermal compression at T_f.
2. Isochoric heating (regeneration).
3. Isothermal expansion at T_c.
4. Isochoric cooling (regeneration).

With a perfect regenerator, its efficiency equals that of Carnot. In practice, it is used in Stirling engines and certain cryocoolers.

1.1.3 Ericsson Cycle

The Ericsson cycle is a reversible cycle consisting of two isotherms and two isobars, with regeneration. Its efficiency is also equal to that of Carnot.

1.1.4 Brayton (Joule) Cycle

Used in gas turbines, it comprises:

1. Adiabatic compression.
2. Isobaric heating.
3. Adiabatic expansion in the turbine.
4. Isobaric cooling.

Its efficiency, for an ideal gas with coefficient γ, is written:

$$\eta_{Brayton} = 1 - \frac{1}{r_p^{(\gamma-1)/\gamma}} \qquad (1.2) \tag{2}$$

where $r_p = P_2/P_1$ is the compression ratio.

1.2 Real Thermal Machines

1.2.1 Internal Combustion Engines

The Beau de Rochas (Otto) cycle models gasoline engines:

1. Intake (isobaric).
2. Adiabatic compression.
3. Combustion (isochoric).
4. Adiabatic expansion.
5. Exhaust (isobaric).

Theoretical efficiency:

$$\eta_{Otto} = 1 - \frac{1}{r^{(\gamma-1)}} \qquad (1.3) \tag{3}$$

where $r = V_{max}/V_{min}$ is the compression ratio.
The Diesel cycle uses combustion at constant pressure, with efficiency:

$$\eta_{\text{Diesel}} = 1 - \frac{1}{r^{(\gamma-1)}} \cdot \frac{\rho^\gamma - 1}{\gamma(\rho - 1)} \qquad (1.4) \tag{4}$$

where $\rho = V_{max}/V_{min}$ at the moment of combustion.

1.2.2 Steam Turbines: Rankine Cycle

The Rankine cycle is used in thermal power plants. It comprises:

1. Adiabatic compression of liquid water (pump).
2. Isobaric heating (boiler) with vaporization.
3. Adiabatic expansion in the turbine.
4. Isobaric condensation.

The efficiency is lower than the Carnot efficiency due to irreversibilities (friction, non-reversible heat transfers).

1.2.3 Refrigerators and Heat Pumps

A refrigerator transfers heat from the cold source to the hot source by consuming work. Its coefficient of performance (COP) is:

$$COP_{frigo} = \frac{Q_f}{W} = \frac{T_f}{T_c - T_f} \quad \text{(Carnot)} \qquad (1.5) \tag{5}$$

For a heat pump:

$$COP_{PAC} = \frac{Q_c}{W} = \frac{T_c}{T_c - T_f} \quad \text{(Carnot)} \qquad (1.6) \tag{6}$$

Real irreversibilities reduce these values.

Part II
Gas Liquefaction and Low Temperatures

2 Gas Liquefaction and Cryogenic Techniques

2.1 Joule-Thomson Effect

During an isenthalpic expansion (Joule-Thomson expansion) through a porous wall or a throttling, the temperature of a real gas may vary. The Joule-Thomson coefficient is defined by:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H \qquad (2.1) \tag{7}$$

- If $\mu_{JT} > 0$: the gas cools as it expands (effect used for liquefaction).
- If $\mu_{JT} < 0$: the gas warms as it expands.
- If $\mu_{JT} = 0$: the temperature remains constant (inversion temperature).

2.2 Linde Cycle

The Linde cycle (or simple expansion cycle) is used to liquefy air. The compressed gas is cooled and then expanded through a Joule-Thomson valve; part of it liquefies, the rest cools the incoming gas in a counter-flow heat exchanger.

2.3 Claude Cycle

The Claude cycle uses an expansion with work production (turbine) in addition to the Joule-Thomson expansion, which improves the liquefaction yield.

2.4 Techniques for Obtaining Low Temperatures

- Adiabatic expansion of a gas (cooling by expansion).
- Joule-Thomson effect (isenthalpic expansion).
- Adiabatic demagnetization: magnetic cooling, used to reach temperatures of the order of a millikelvin.
- Cooling by evaporation of helium: allows reaching 0.3 K.

- ^{3}He-^{4}He dilution: used to reach a few millikelvins.
- Laser cooling: used to reach temperatures of the order of a microkelvin.

Table 1: Cryogenic techniques and temperatures reached

Technique	**Temperature reached**
Linde cycle (liquid air)	77 K (nitrogen)
Liquid helium	4.2 K
Cooling by evaporation of ^{4}He	1 K
Cooling by evaporation of ^{3}He	0.3 K
^{3}He-^{4}He dilution	$\sim$ 2 mK
Nuclear adiabatic demagnetization	$\sim$ 1 μK
Laser cooling	$\sim$ 100 nK

Part III
Phase Transitions

3 Phase Transitions

3.1 Phase Transitions of a Pure Substance

3.1.1 Ehrenfest Classification

Phase transitions are classified according to the order of the derivative of the free enthalpy G that exhibits a discontinuity:

- **First-order transition (order 1)**: discontinuity of $S = -(\partial G/\partial T)_P$ and $V = (\partial G/\partial P)_T$. There is latent heat and volume variation. Example: fusion, vaporization, sublimation.
- **Second-order transition (order 2)**: continuity of S and V, but discontinuity of C_P, κ_T, α. No latent heat. Example: ferromagnetic-paramagnetic transition, superconducting transition, order-disorder transition.

3.1.2 Clausius-Clapeyron Equation

For a first-order transition, the coexistence curve obeys:

$$\frac{dP}{dT} = \frac{L}{T\Delta v} \qquad (3.1) \tag{8}$$

where L is the latent heat and Δv the variation of molar volume.
For vaporization, assuming the vapor is ideal and neglecting v_{liq}:

$$\frac{d\ln P}{dT} = \frac{L_{vap}}{RT^2} \qquad (3.2) \tag{9}$$

3.1.3 Critical Point

Beyond the critical point (T_c, P_c), the liquid/gas distinction disappears. Critical parameters for some substances:

Table 2: Critical parameters of some substances

Substance	T_c **(K)**	P_c **(bar)**	v_c **(cm^3·mol^{-1})**
Water (H_2O)	647.1	220.6	56.0
Carbon dioxide (CO_2)	304.1	73.8	94.0
Ammonia (NH_3)	405.5	113.3	72.5
Oxygen (O_2)	154.6	50.4	73.4
Nitrogen (N_2)	126.2	33.9	89.2
Helium (^{4}He)	5.2	2.3	57.8

3.2 Phase Transitions of a Mixture

3.2.1 Gibbs Phase Rule

For a system with C constituents and P phases in equilibrium, the variance (number of degrees of freedom) is:

$$v = C - P + 2 \qquad (3.3) \tag{10}$$

The factor 2 corresponds to T and P.

3.2.2 Binary Diagrams

For a binary mixture ($C = 2$), the phase diagrams present liquid, vapor, and two-phase regions. The dew and bubble curves delimit these regions. Raoult's law for ideal solutions is written:

$$p_i = x_i p_i^*(T) \qquad (3.4) \tag{11}$$

where p^* is the saturated vapor pressure of the pure constituent i.
Dalton's law relates the partial pressures to the total pressure: $P = \sum_i p_i$.

3.2.3 Azeotrope

An azeotrope is a mixture whose liquid and vapor compositions are identical at equilibrium. It behaves like a pure substance for distillation (example: ethanol-water at 95.6%).

3.3 Dilute Solutions

3.3.1 Raoult's Law

For an ideal solution, the partial pressure of the solvent is:

$$p_A = x_A p_A^* \qquad (3.5) \tag{12}$$

The lowering of vapor pressure is:

$$\Delta p = p_A^* - p_A = x_B p_A^* \qquad (3.6) \tag{13}$$

where x_B is the mole fraction of the solute.

3.3.2 Cryoscopy and Ebullioscopy Laws

The addition of a non-volatile solute lowers the freezing point and raises the boiling point of the solvent:

$$\Delta T_{fus} = -K_f m_B \quad \text{(cryoscopic lowering)} \tag{3.7}$$
$$\Delta T_{eb} = +K_e m_B \quad \text{(ebullioscopic elevation)} \tag{3.8}$$

where m_B is the molality of the solute, and K_f, K_e are constants characteristic of the solvent:

$$K_f = \frac{RT_{fus}^2 M_A}{\Delta H_{fus}}, \quad K_e = \frac{RT_{eb}^2 M_A}{\Delta H_{vap}} \tag{3.9}$$

3.3.3 Osmotic Pressure

The osmotic pressure Π of a dilute solution is given by van't Hoff's law:

$$\Pi = \frac{n_B}{V} RT = c_B RT \tag{3.10}$$

where c_B is the molar concentration of the solute. This law is essential in biology (membrane transport) and polymer chemistry.

3.4 Chemical Equilibrium

3.4.1 Law of Mass Action

For a reaction $\sum_i \nu_i A_i = 0$ in a perfect gas phase, the equilibrium constant in partial pressures is:

$$K_P(T) = \prod_i \left(\frac{p_i}{p_0}\right)^{\nu_i} = \exp\left(-\frac{\Delta_r G^\circ(T)}{RT}\right) \tag{3.11}$$

For an ideal solution, mole fractions are used:

$$K_x(T, P) = \prod_i x_i^{\nu_i} \tag{3.12}$$

3.4.2 van't Hoff Relation

The variation of K_P with temperature is given by:

$$\frac{d \ln K_P}{dT} = \frac{\Delta_r H^\circ}{RT^2} \qquad (3.13) \tag{14}$$

Integrating (assuming $\Delta_r H^\circ$ constant):

$$\ln\left(\frac{K_P(T_2)}{K_P(T_1)}\right) = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (3.14) \tag{15}$$

3.4.3 Le Chatelier's Principle

A perturbation of equilibrium (variation of T, P, concentration) causes the system to evolve so as to oppose this perturbation:

- Increase in T: displacement in the endothermic direction.
- Increase in P: displacement toward the side with the fewest gaseous moles.

- Addition of a reactant: displacement in the direction of its consumption.

Part IV
Thermodynamics of Magnetic Materials

4 Thermodynamics of Magnetic Materials

4.1 Macroscopic Approach

4.1.1 Magnetic Quantities

For a magnetic material subjected to an external magnetic field H ($\mathrm{A{\cdot}m^{-1}}$), we define:

- The magnetization M ($\mathrm{A{\cdot}m^{-1}}$), magnetic moment per unit volume.
- The magnetic induction $B = \mu_0(H + M)$ (T).
- The magnetic susceptibility $\chi = M/H$ (dimensionless).
- The relative permeability $\mu_r = 1 + \chi$.

4.1.2 Fundamental Relation

The elementary magnetic work received by the system is:

$$\delta W_{mag} = \mu_0 H \, dM \qquad (4.1) \tag{16}$$

The differential of internal energy becomes:

$$dU = T \, dS + \mu_0 H \, dM \qquad (4.2) \tag{17}$$

By Legendre transformation, we define:

$$\text{Magnetic enthalpy: } U - \mu_0 H M \tag{4.3}$$
$$\text{Magnetic free energy: } F(T, M) = U - TS \tag{4.4}$$
$$\text{Magnetic free enthalpy: } G(T, H) = U - TS - \mu_0 H M \tag{4.5}$$

with:

$$dG = -S \, dT - \mu_0 M \, dH \qquad (4.6) \tag{18}$$

We deduce:

$$M = -\frac{1}{\mu_0} \left(\frac{\partial G}{\partial H} \right)_T \qquad (4.7) \tag{19}$$

4.1.3 Curie and Curie-Weiss Laws

For a paramagnetic material, Curie's law is written:

$$\chi = \frac{C}{T} \qquad (4.8) \tag{20}$$

where C is the Curie constant.
For a ferromagnetic material above the Curie temperature T_C, the Curie-Weiss law applies:

$$\chi = \frac{C}{T - T_C} \qquad (4.9) \tag{21}$$

4.1.4 Magnetocaloric Effect

The adiabatic application or removal of a magnetic field modifies the temperature of a magnetic material. The magnetocaloric coefficient is:

$$\left(\frac{\partial T}{\partial H}\right)_S = -\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H \qquad (4.10) \tag{22}$$

This effect is used for magnetic refrigeration, an ecological alternative to conventional refrigerants.

4.2 Microscopic Model and Analytical Solution

4.2.1 Ising Model

The Ising model describes a lattice of interacting spins $\sigma_i = \pm 1$. The Hamiltonian is written:

$$\mathcal{H} = -J\sum_{\langle i,j\rangle}\sigma_i\sigma_j - h\sum_i \sigma_i \qquad (4.11) \tag{23}$$

where J is the exchange energy, $h = \mu_B H/k_B T$ the reduced field, and $\langle i,j\rangle$ denotes pairs of nearest neighbors.

4.2.2 Mean-Field Approximation

In the mean-field approximation, the interaction of each spin with its neighbors is replaced by an interaction with a mean field proportional to the average magnetization $m = \langle\sigma\rangle$. The self-consistent equation becomes:

$$m = \tanh\left(\frac{Jzm + h}{k_B T}\right) \qquad (4.12) \tag{24}$$

where z is the number of neighbors.

In the absence of an external field ($h = 0$), a ferromagnetic-paramagnetic transition is obtained for:

$$k_B T_C = zJ \qquad (4.13) \tag{25}$$

4.2.3 Brillouin Function

For spins of moment J (in units of $\hbar$), the average magnetization is given by the Brillouin function:

$$M = ng\mu_B J\, B_J(x), \quad x = \frac{g\mu_B JH}{k_B T} \qquad (4.14) \tag{26}$$

where:

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right) \qquad (4.15) \tag{27}$$

- For $x \ll 1$: $B_J(x) \approx \frac{J+1}{2J}x$, which recovers Curie's law.
- For $x \gg 1$: $B_J(x) \to 1$ (saturation).

4.2.4 Analytical Solution: Two-Level Model ($J = 1/2$)

For a spin 1/2, the Brillouin function simplifies to $\tanh(x/2)$. The magnetization is written:

$$M = n\mu \tanh\left(\frac{\mu H}{k_B T}\right) \qquad (4.16) \tag{28}$$

where μ is the magnetic moment. The susceptibility in the weak-field limit follows Curie's law:

$$\chi = \frac{n\mu^2}{k_B T} \qquad (4.17) \tag{29}$$

4.2.5 Langevin Model (Classical Spins)

For classical magnetic moments that can take all orientations, the Langevin function is obtained:

$$L(x) = \coth(x) - \frac{1}{x}, \quad M = n\mu\, L\left(\frac{\mu H}{k_B T}\right) \qquad (4.18) \tag{30}$$

In the weak-field limit: $M \approx \dfrac{n\mu^2 H}{3k_B T}$ (classical Curie law).

Chapter Summary

Table 3: Summary of the applications of Chapter 7

Theme	**Essential idea**
Carnot cycle	$\eta = 1 - T_f/T_c$, maximum efficiency.
Stirling, Ericsson cycles	Reversible cycles with regeneration.
Otto, Diesel, Brayton, Rankine cycles	Modeling of real engines.
Refrigerator COP	$COP = T_f/(T_c - T_f)$.
Joule-Thomson effect	$\mu_{JT} = (\partial T/\partial P)_H$, basis of liquefaction.
Cryogenics	Expansion, demagnetization, ^{3}He-^{4}He dilution, laser.
1st/2nd order transitions	Latent heat vs discontinuity of C_P.
Clausius-Clapeyron	$dP/dT = L/(T\Delta v)$.
Critical point	Disappearance of the liquid/gas distinction.
Gibbs rule	$v = C - P + 2$ (variance).
Raoult's law	$p_i = x_i p_i^*$ (ideal solutions).
Cryoscopy/ebullioscopy	$\Delta T = K m_B$.
Osmotic pressure	$\Pi = c_B RT$.
Law of mass action	$K_P = \prod (p_i/P^\circ)^{\nu_i}$.
van't Hoff	$d\ln K_P/dT = \Delta_r H^\circ/RT^2$.
Macroscopic magnetism	$dG = -SdT - \mu_0 M dH$.
Curie / Curie-Weiss laws	$\chi = C/T$ or $\chi = C/(T - T_C)$.
Magnetocaloric effect	Magnetic refrigeration.
Ising model	$\mathcal{H} = -J\sum \sigma_i\sigma_j - h\sum \sigma_i$.
Mean field	$m = \tanh((Jzm + h)/k_B T)$.
Brillouin function	$M = ng\mu_B J B_J(x)$.