Preparing for the Physics GRE: Day 2
Statistical Mechanics and Thermodynamics

Daniel T. Citron

dtc65@cornell.edu

2/25/15

http://greprep.dtcitron.com

Outline:

- Statistical mechanics
  - Probabilistic thinking in classical physics
  - Partition function
  - Entropy
  - Quantum statistical mechanics
- Blackbody Radiation
- Thermodynamics
  - First law
  - Ideal gas processes
  - Second law

Statistical Mechanics

Probabilistic Thinking

- An example problem:

15. A sample of N atoms of helium gas is confined in a 1.0 cubic meter volume. The probability that none of the helium atoms is in a 1.0×10^{-6} cubic meter volume of the container is

    (A) 0 (B) $(10^{-6})^N$ (C) $(1 - 10^{-6})^N$

    (D) $1 - (10^{-6})^N$ (E) 1

- Just need to consider the probability of placing all N particles outside the tiny excluded volume

- P(Outside) = 1-P(Inside) = $1-10^{-6}$

- Placement of each of the N atoms is independent of the placement of the others

- => P(Outside)^N = $(1-10^{-6})^N$

- Alternatively: take limits! Should the probability be big or small as N approaches infinity?

Probabilistic Thinking

- Classical mechanics is purely deterministic
- Laplace: can perfectly describe everything given enough time
- For many $O(10^{23})$ degrees of freedom, phase space becomes too complicated to describe exactly
- If we can't describe the system exactly, let's describe it probabilistically
- So we posit:
  - System is constantly exploring phase space, moving from state to state
  - Given that the system has fixed energy, all states with that energy are available to the system
  - The system spends an equal amount of time in each of these states (probabilities of each of these states are identical)

Maxwell-Boltzmann Probability Weights

- What is the probability that the system will be found in a state with energy E?

- Boltzmann weights: $P(E) \propto e^{-E/kT} = e^{-\beta E}$

- Can use Boltzmann weights to find the relative probabilities of being found in two states

- Think of temperature as a parameter that controls the frequency at which the system jumps from a lower energy state to a higher energy state

Maxwell-Boltzmann Probability Weights

- Example problem:

77. An ensemble of systems is in thermal equilibrium
    with a reservoir for which $kT = 0.025$ eV.
    State A has an energy that is 0.1 eV above that
    of state B. If it is assumed the systems obey
    Maxwell-Boltzmann statistics and that the
    degeneracies of the two states are the same, then
    the ratio of the number of systems in state A to
    the number in state B is

    (A) e^{+4}

    (B) $e^{+0.25}$

    (C) 1

    (D) $e^{-0.25}$

    (E) e^{-4}

$$P(A) \propto e^{-\beta(E+.1eV)}$$

$$P(B) \propto e^{-\beta(E)}$$

$$P(A)/P(B) = e^{-.1eV/(.025eV)} = e^{-4}$$

Partition Function

- Suppose we know the energy E for each system configuration σ
- Sum MB factors over all possible system configurations {σ}

$$z = \sum_{\{\sigma\}} e^{-\beta E(\sigma)}$$

- (Note possibility of degeneracy, where many σ's produce same E)
- Observations: Take limits!
  - kT-> 0
  - kT >> E

67. A large isolated system of N weakly interacting particles is in thermal equilibrium. Each particle has only 3 possible nondegenerate states of energies 0, ϵ, and 3ϵ. When the system is at an absolute temperature $T >> \epsilon/k$, where k is Boltzmann's constant, the average energy of each particle is

(A) 0   (B) ϵ (C) $\frac{4}{3}\epsilon$ (D) 2ϵ (E) 3ϵ

Partition Function

A system in thermal equilibrium at temperature T consists of a large number N_0 of subsystems, each of which can exist only in two states of energy E_1 and E_2, where $E_2 - E_1 = \epsilon > 0$. In the expressions that follow, k is the Boltzmann constant.

71. For a system at temperature T, the average number of subsystems in the state of energy E_1 is given by

(A) $\dfrac{N_0}{2}$

(B) $\dfrac{N_0}{1 + e^{-\epsilon/kT}}$

(C) $N_0 e^{-\epsilon/kT}$

(D) $\dfrac{N_0}{1 + e^{\epsilon/kT}}$

(E) $\dfrac{N_0 e^{\epsilon/kT}}{2}$

$$z = \sum_{\{\sigma\}} e^{-\beta E(\sigma)} = e^{-\beta E_1} + e^{-\beta E_2}$$

$$P(\sigma | E(\sigma) = E_1) = e^{-\beta E_1}/z = \frac{e^{-\beta E_1}}{e^{-\beta E_1} + e^{-\beta E_2}} = \frac{1}{1 + e^{-\beta(E_2 - E_1)}}$$

Partition Function

- Contains an incredible amount of information
- We don't measure z, we measure its moments:
  - Average system energy is found:

$$\langle E \rangle = \sum_{\{\sigma\}} E(\sigma) e^{-\beta E(\sigma)} / z \qquad z = \sum_{\{\sigma\}} e^{-\beta E(\sigma)}$$

$$-\frac{\partial}{\partial \beta} \sum_{\{\sigma\}} e^{-\beta E(\sigma)} = \sum_{\{\sigma\}} E(\sigma) e^{-\beta E(\sigma)}$$

$$\Rightarrow \langle E \rangle = -\frac{\partial}{\partial \beta} \log \sum_{\{\sigma\}} e^{-\beta E(\sigma)} = -\frac{\partial}{\partial \beta} \log z$$

- Question:
  - What is the average height of a single molecule of air with mass m?
  - (Note: Can also answer with dimensional analysis only)

Partition Function

- Question:
  - What is the average height of a single molecule of air with mass m?
  - (Note: Can also answer with dimensional analysis only)

$$\Rightarrow \ \langle E \rangle = -\frac{\partial}{\partial \beta} \log \sum_{\{\sigma\}} e^{-\beta E(\sigma)} = -\frac{\partial}{\partial \beta} \log z$$

$$z = \sum_h e^{-\beta mgh} \propto \int_0^{\infty} e^{-\beta mgh} = \frac{1}{\beta mg}$$

$$\langle E \rangle = mg \langle h \rangle = -\frac{\partial}{\partial(\beta mg)} \log \frac{1}{\beta mg} = \beta mg = \frac{mg}{kT}$$

Heat Capacity and Response Functions

- Response functions measure how a macroscopic property of the system changes when a control parameter is varied
- Calculated using derivatives of the partition function
- Heat capacity: How much energy does it take to raise the temperature of an object?
  - [C] = Joule/Kelvin

$$C = \frac{\partial}{\partial T}\langle E \rangle = k\beta^2 \frac{\partial^2}{\partial \beta^2} \log z$$

- Magnetic susceptibility
  - How much does the magnetization change given an applied field?

$$\chi = \frac{\partial}{\partial B}\langle M \rangle = -\frac{\partial^2}{\partial B^2} \log z$$

- Thermal expansion (V vs. T)
- Isothermal compressibility (V vs P)

72. The internal energy of this system at any temperature T is given by $E_1 N_0 + \dfrac{N_0\epsilon}{1 + e^{\epsilon/kT}}$. The heat capacity of the system is given by which of the following expressions?

(A) $N_0 k \left(\dfrac{\epsilon}{kT}\right)^2 \dfrac{e^{\epsilon/kT}}{(1 + e^{\epsilon/kT})^2}$

(B) $N_0 k \left(\dfrac{\epsilon}{kT}\right)^2 \dfrac{1}{(1 + e^{\epsilon/kT})^2}$

(C) $N_0 k \left(\dfrac{\epsilon}{kT}\right)^2 e^{-\epsilon/kT}$

(D) $\dfrac{N_0 k}{2} \left(\dfrac{\epsilon}{kT}\right)^2$

(E) $\dfrac{3}{2} N_0 k$

Equipartition Theorem

- Every degree of freedom ξ that adds ξ^2 dependence to the Hamiltonian adds $\frac{1}{2}kT$ to the average energy, $\frac{1}{2}k$ to C_v

- Common questions include average energy of monatomic or diatomic gases => count the degrees of freedom relevant to the Hamiltonian

- Note temperature dependence of vibrational and rotational modes (only excited at high temperatures)

87. In a gas of N diatomic molecules, two possible models for a classical description of a diatomic molecule are:

Model I	Model II
O———O	O-wwwww-O
Rigid Dumbbell	Springy Dumbbell
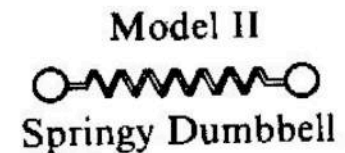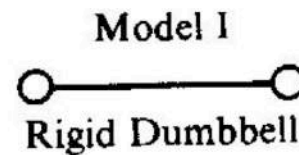
Which of the following statements about this gas is true?

(A) Model I has a specific heat $c_v = \frac{3}{2}Nk$.

(B) Model II has a smaller specific heat than Model I.

(C) Model I is always correct.

(D) Model II is always correct.

(E) The choice between Models I and II depends on the temperature.

Entropy

- Microscopic:
  - Entropy measures disorder and ignorance: How difficult is it to make a prediction?
  - More available states makes it difficult to predict the specific state
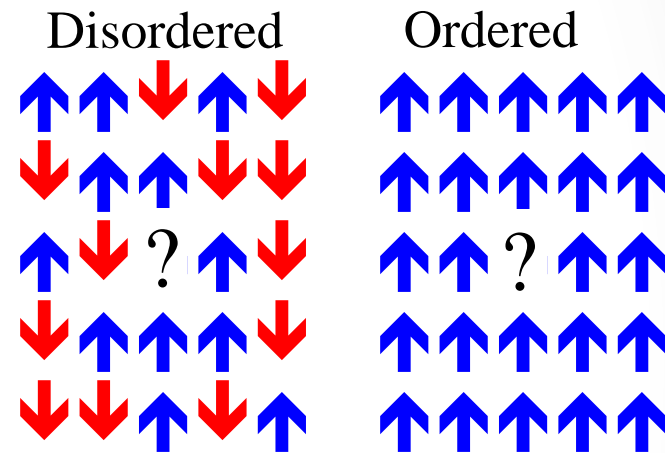
  $$S \sim \log \Omega_{\#states}$$

- Macroscopic

  $$F = E - TS$$

  - In real world systems, we minimize free energy
  - Maximize entropy as energy is minimized

Ising Model Phases:

Disordered   Ordered

In which case is the missing spin's state easier to predict?

Entropy: Probabilistic Interpretation

- Entropy is maximized when there is maximal ignorance about the state of the system
  - Macroscopically, the system reaches equilibrium is in the most probable state, which has the largest number of available microstates
  - For systems with many, many degrees of freedom, it becomes vanishingly unlikely that the system will spontaneously switch to a lower-probability, lower-entropy state
- Shannon entropy: $\quad S = -k \sum_{\sigma} p_{\sigma} \log p_{\sigma}$

63. Which of the following is true if the arrangement of an isolated thermodynamic system is of maximal probability?

(A) Spontaneous change to a lower probability occurs.
(B) The entropy is a minimum.
(C) Boltzmann's constant approaches zero.
(D) No spontaneous change occurs.
(E) The entropy is zero.

Relating Entropy to Partition Function

- Try: plug MB weights into the probabilistic interpretation of entropy
- Results in familiar expression for free energy

$$S = -k \sum_{\sigma} p_{\sigma} \log p_{\sigma}$$

$$S = -k \sum_{\sigma} e^{-\beta E} (\log e^{-\beta E} - \log z)/z$$

$$S = -k(\beta \langle E \rangle + \log z)$$

$$\Rightarrow F \equiv -\log z = E - TS$$

A system in thermal equilibrium at temperature T consists of a large number N_0 of subsystems, each of which can exist only in two states of energy E_1 and E_2, where $E_2 - E_1 = \epsilon > 0$. In the expressions that follow, k is the Boltzmann constant.

73. Which of the following is true of the entropy of the system?

(A) It increases without limit with T from zero at $T = 0$.

(B) It decreases with increasing T.

(C) It increases from zero at $T = 0$ to $N_0 k \ln 2$ at arbitrarily high temperatures.

(D) It is given by $N_0 k \left[\frac{5}{2} \ln T - \ln p + \text{constant} \right]$.

(E) It cannot be calculated from the information given.

Relating Entropy to Partition Function

- Calculation:
  - Use: $S = -k(\beta \langle E \rangle + \log z)$
  - As T->∞, β->0
  - Need to calculate z:

  $$z = e^{-\beta E_1} + e^{-\beta E_2} \rightarrow e^0 + e^0 = 2$$

A system in thermal equilibrium at temperature T consists of a large number N_0 of subsystems, each of which can exist only in two states of energy E_1 and E_2, where $E_2 - E_1 = \epsilon > 0$. In the expressions that follow, k is the Boltzmann constant.

73. Which of the following is true of the entropy of the system?

(A) It increases without limit with T from zero at $T = 0$.

(B) It decreases with increasing T.

(C) It increases from zero at $T = 0$ to $N_0 k \ln 2$ at arbitrarily high temperatures.

(D) It is given by $N_0 k \left[\frac{5}{2} \ln T - \ln p + \text{constant} \right]$.

(E) It cannot be calculated from the information given.

- Intuition:

  (D): is for ideal gases

  (B): Higher temperature means higher probability of jumping between states => more disorder and entropy

  (A) & (C): For high temperatures, we know all energy states approach equal probability, so there probably a finite cutoff instead of a boundless increase

Quantum Statistical Mechanics

72. Which of the following statements about bosons and/or fermions is true?

(A) Bosons have symmetric wave functions and obey the Pauli exclusion principle.
(B) Bosons have antisymmetric wave functions and do not obey the Pauli exclusion principle.
(C) Fermions have symmetric wave functions and obey the Pauli exclusion principle.
(D) Fermions have antisymmetric wave functions and obey the Pauli exclusion principle.
(E) Bosons and fermions obey the Pauli exclusion principle.

Quantum Statistical Mechanics

- Fermions obey the Pauli Exclusion Principle:
  - No two can occupy the same state at the same time
  - Occupation numbers $n_f = 0$ or 1
  - Creates "degeneracy pressure" in a Fermionic gas
- No restriction on Boson occupation numbers:
  - $n_b = 0, 1, 2, 3$, etc.
- Average occupation number of states by Bosons and Fermions with energy E:

$$\langle n_E \rangle_{Bosons} = \frac{1}{e^{\beta(E-\mu)} - 1}$$

$$\langle n_E \rangle_{Fermions} = \frac{1}{e^{\beta(E-\mu)} + 1}$$

$$\langle n_E \rangle_{Classical} = \frac{1}{e^{\beta(E-\mu)} + 0} = e^{-\beta(E-\mu)}$$

88. Consider a system of N noninteracting particles confined in a volume V at a temperature such that the particles obey classical Boltzmann statistics. If the temperature is lowered to the point at which quantum effects become important, the pressure of the gas may differ depending on whether the particles are fermions or bosons. Let P_F be the pressure exerted by the particles if they are fermions, P_B be the pressure if they are bosons, and P_C be the pressure the particles would exert if quantum effects are ignored. Which of the following is true?

(A) $P_F = P_B = P_C$

(B) $P_F > P_C > P_B$

(C) $P_F > P_B > P_C$

(D) $P_F < P_B < P_C$

(E) $P_F < P_C < P_B$

Blackbody Radiation

- Radiation from a body at thermodynamic equilibrium with its surroundings
- Treats object as a gas of discrete bosonic photons
- Absorbs all incoming photons, emits photons on continuous spectrum
- Examples
  - The Sun
  - Your body in outer space
- Characteristic spectrum (W/m²/s/steradian)

$$B(\lambda, T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{(h\nu/k_B T)} - 1}$$
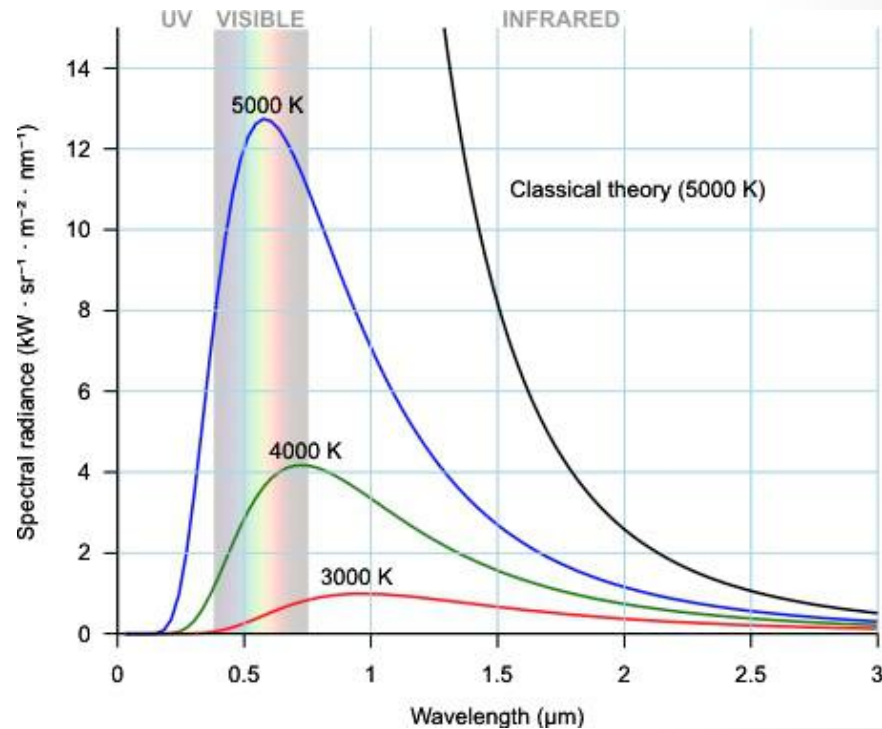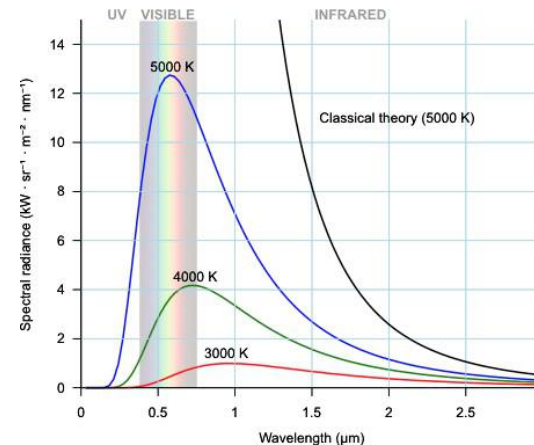

http://en.wikipedia.org/wiki/Black-body_radiation

Rules to Remember

- Scaling of total energy flux ($J/m^2/s$) vs temperature (Stefan-Boltzmann Law)

$$J = \sigma T^4, \qquad \sigma = 5.67 \times 10^{-8} \ Wm^{-2}K^{-4}$$

- Scaling of spectrum peak wavelength vs temperature (Wien's Law)

$$\lambda_{max} = bT^{-1}$$

Statistical Mechanics Summary

- Maxwell-Boltzmann probability weights
- Partition Function
- Calculating expectation values using the partition function
- Entropy
- Quantum statistical mechanics
  - Bosons, Fermions, classical particles
  - Blackbody radiation
- Additional concepts
  - **Free electron gas**
  - **Diffusion equation**
  - Heat capacity and response functions
  - Equipartition theorem
  - Blackbody radiation

Thermodynamics

Heat Exchange

- Heat is *energy* exchanged between the system and the reservoir it is coupled to
  - Heat has units of energy: [Q]= J
  - Temperature is a completely different parameter
- Heat capacity is the amount of energy required to raise the system temperature: [C] = J/K

14. Two identical 1.0-kilogram blocks of copper metal, one initially at a temperature $T_1 = 0°$ C and the other initially at a temperature $T_2 = 100°$ C, are enclosed in a perfectly insulating container. The two blocks are initially separated. When the blocks are placed in contact, they come to equilibrium at a final temperature T_f. The amount of heat exchanged between the two blocks in this process is equal to which of the following? (The specific heat of copper metal is equal to 0.1 kilocalorie/kilogram °K.)

(A) 50 kcal
(B) 25 kcal
(C) 10 kcal
(D) 5 kcal
(E) 1 kcal

Ideal Gas Properties

- Isochoric: V is constant dV = 0
- Isobaric: P is constant dP = 0
- Isothermal: T is constant dT = 0
- Adiabatic: no heat exchange dQ = 0
- **NB**: U of an _ideal_ gas depends _only_ on temperature

$$PV = nRT$$

$$C_V = \frac{\partial Q}{\partial T} \Rightarrow \Delta Q = nC_V \Delta T$$

Process	ΔQ	ΔW	ΔU=ΔQ-ΔW
Isochoric	$nC_V\Delta T$	0	$nC_V\Delta T$
Isobaric	$nC_P\Delta T$	$P\Delta V = nR\Delta T$	$nC_P\Delta T - nR\Delta T$ $= nC_V\Delta T$
Isothermal	$Q = W$ $= nRT\log(V_2/V_1)$	$nRT\log(V_2/V_1)$	$0, \Delta U \sim \Delta T$
Adiabatic	0	$\Delta U = -\Delta W$ $= -nC_V\Delta T$	$nC_V\Delta T$

1st Law of Thermodynamics

- Equivalent to Conservation of Energy:
  - Change in system internal energy is equal to the heat input minus the work done by the system:

$$dU=dQ-dW$$

- Heat exchange definition: $dQ=TdS$

- Work done <u>by</u> the system on surroundings: $dW=-\vec{J}\cdot\vec{dx}$
  - J and x are "conjugate variables" with [Jx] = Energy
  - J is generalized force, x is generalized displacement
  - Ex: P and V; μ and N; B and M

- So the 1st law becomes $dU=TdS+\vec{J}\cdot\vec{dx}$

- Example:
  - Ideal gas in contact with heat bath and particle reservoir:

$$dU=TdS+PdV+\mu dN$$

1st Law: Manipulating Differentials

- The trick for many problems is manipulating differentials
- (Probably do not need to memorize all the Maxwell relations)
- Use dimensional analysis
- Check: what are you keeping constant?

- For example, use the first law
  to recover the formal definition
  of temperature

$$dU=TdS+PdV+\mu dN$$

66. For a system in which the number of particles is fixed, the reciprocal of the Kelvin temperature T is given by which of the following derivatives? (Let P = pressure, V = volume, S = entropy, and U = internal energy.)

(A) $\left(\frac{\partial P}{\partial V}\right)_S$

(B) $\left(\frac{\partial P}{\partial S}\right)_V$

(C) $\left(\frac{\partial S}{\partial P}\right)_U$

(D) $\left(\frac{\partial V}{\partial P}\right)_U$

(E) $\left(\frac{\partial S}{\partial U}\right)_V$

1st Law: Manipulating Differentials

- Another example: what is the difference between heat capacities C_P and C_V?

14. For an ideal gas, the specific heat at constant pressure C_p is greater than the specific heat at constant volume C_v because the
(A) gas does work on its environment when its pressure remains constant while its temperature is increased
(B) heat input per degree increase in temperature is the same in processes for which either the pressure or the volume is kept constant
(C) pressure of the gas remains constant when its temperature remains constant
(D) increase in the gas's internal energy is greater when the pressure remains constant than when the volume remains constant
(E) heat needed is greater when the volume remains constant than when the pressure remains constant

$$dU=dQ+PdV \qquad\qquad PV=nRT$$

1st Law: Manipulating Differentials

14. For an ideal gas, the specific heat at constant pressure C_p is greater than the specific heat at constant volume C_v because the

    (A) gas does work on its environment when its pressure remains constant while its temperature is increased
    (B) heat input per degree increase in temperature is the same in processes for which either the pressure or the volume is kept constant
    (C) pressure of the gas remains constant when its temperature remains constant
    (D) increase in the gas's internal energy is greater when the pressure remains constant than when the volume remains constant
    (E) heat needed is greater when the volume remains constant than when the pressure remains constant

$$dU=dQ+PdV$$

$$PV=nRT$$

- Holding V constant, dV = 0

$$C_V=\left(\frac{\partial U}{\partial T}\right)_V=\frac{\partial Q}{\partial T}$$

- Holding P constant, there's an extra term from $PdV \neq 0$

$$C_P=\left(\frac{\partial U}{\partial T}\right)_P=\frac{\partial Q}{\partial T}+P\frac{\partial V}{\partial T}=C_V+nR > C_V$$

- From intuition:

  (B): this would mean $C_P=C_V$

  (C): ?

  (D): ideal gas energy depends on T only

  (E): (begging the question)

1st Law: Ideal Gas Processes

- Isotherms in P-V state space
  - Holding T constant, the Ideal Gas Law tells us PV = Constant
- Adiabats in P-V state space
  - Integrate: $nC_V dT = -PdV = nRTdV/V$
  - We use $\gamma = C_P/C_V$
  - => PV^γ = Constant
- An example problem:

6. An ideal monatomic gas expands quasi-statically to twice its volume. If the process is isothermal, the work done by the gas is W_i. If the process is adiabatic, the work done by the gas is W_a. Which of the following is true?
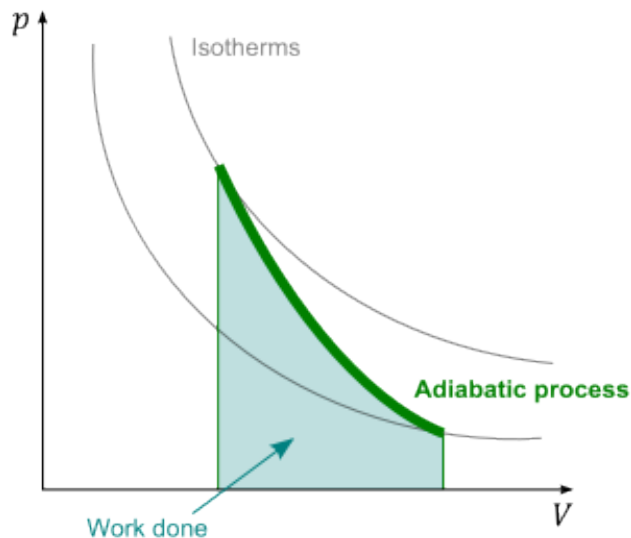
(A) $W_i = W_a$
(B) $0 = W_i < W_a$
(C) $0 < W_i < W_a$
(D) $0 = W_a < W_i$
(E) $0 < W_a < W_i$

(An additional example)

73. The adiabatic expansion of an ideal gas is described by the equation $PV^\gamma = C$, where γ and C are constants. The work done by the gas in expanding adiabatically from the state (V_i, P_i) to (V_f, P_f) is equal to

(A) $P_f V_f$

(B) $\dfrac{(P_i + P_f)}{2}(V_f - V_i)$

(C) $\dfrac{P_f V_f - P_i V_i}{1 - \gamma}$

(D) $\dfrac{P_i(V_f^{1+\gamma} - V_i^{1+\gamma})}{1 + \gamma}$

(E) $\dfrac{P_f(V_f^{1-\gamma} - V_i^{1-\gamma})}{1 + \gamma}$

1st Law: Ideal Gas Processes

6. An ideal monatomic gas expands quasi-statically to twice its volume. If the process is isothermal, the work done by the gas is W_i. If the process is adiabatic, the work done by the gas is W_a. Which of the following is true?

(A) $W_i = W_a$
(B) $0 = W_i < W_a$
(C) $0 < W_i < W_a$
(D) $0 = W_a < W_i$
(E) $0 < W_a < W_i$

- Isotherms: PV = Constant

$$W = \int P dV = \int \frac{nrT}{V} dV = nrT \log 2$$

- Adiabats: PV^γ = Constant

$$W = \int P dV = \int \frac{C}{V^\gamma} dV = \frac{C}{1-\gamma} V^\gamma (2^\gamma - 1) \approx .55 nRT$$

Isotherms

Adiabatic process

Work done

p

V

Entropy in Thermodynamics

- Formal definition of temperature given by the following (at equilibrium, holding all other parameters constant)

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

- Recall: relation between heat exchange and entropy

$$dQ = TdS$$

74. A body of mass m with specific heat C at temperature 500 K is brought into contact with an identical body at temperature 100 K, and the two are isolated from their surroundings. The change in entropy of the system is equal to

(A) $(4/3)mC$
(B) $mC\ln(9/5)$
(C) $mC\ln(3)$
(D) $-mC\ln(5/3)$
(E) 0

- What is the change in heat?

$$dQ = mCdT$$

- What is the *total* change in entropy?

$$dS = \int \frac{dQ}{T} = \int \frac{mCdT}{T}$$

$$dS_1 + dS_2 = \int_{100}^{300} \frac{mCdT}{T} + \int_{500}^{300} \frac{mCdT}{T}$$

$$= mC(\log 3 - \log 5/3)$$

Engine Cycles

- Imagine a box of gas subject to a series of changes in pressure, temperature, volume, etc

- Draw the series of changes as a trajectory in the P-V plane

- Gas internal energy depends on T only:
  - If it returns to original state, no net change in energy

- Work done is the area enclosed by the cycle
  - Heat exchange with environment = Work done
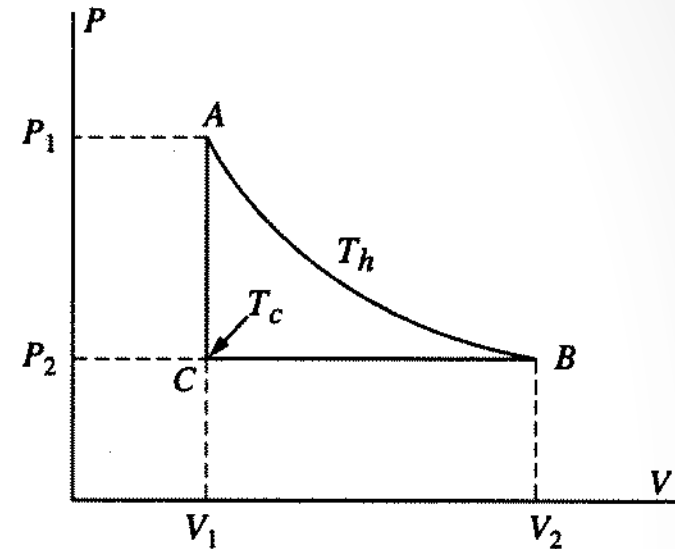
15. Suppose one mole of an ideal gas undergoes the reversible cycle $ABCA$ shown in the P-V diagram above, where AB is an isotherm. The molar heat capacities are C_p at constant pressure and C_v at constant volume. The net heat added to the gas during the cycle is equal to

(A) $RT_h V_2/V_1$

(B) $-C_p(T_h - T_c)$

(C) $C_v(T_h - T_c)$

(D) $RT_h \ln V_2/V_1 - C_p(T_h - T_c)$

(E) $RT_h \ln V_2/V_1 - R(T_h - T_c)$

Engine Cycles
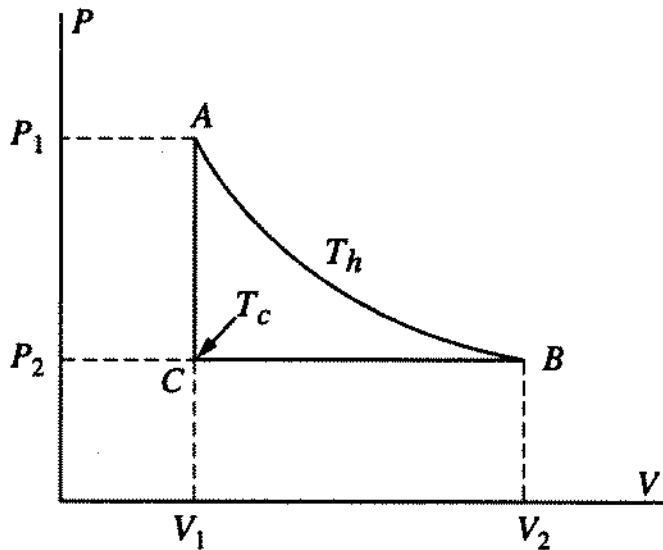
15. Suppose one mole of an ideal gas undergoes the reversible cycle *ABCA* shown in the *P-V* diagram above, where *AB* is an isotherm. The molar heat capacities are C_p at constant pressure and C_v at constant volume. The net heat added to the gas during the cycle is equal to

(A) $RT_h V_2/V_1$

(B) $-C_p(T_h-T_c)$

(C) $C_v(T_h-T_c)$

(D) $RT_h \ln V_2/V_1 - C_p(T_h-T_c)$

(E) $RT_h \ln V_2/V_1 - R(T_h-T_c)$

- Total change in energy during one cycle?
- Use 1st Law: $Q = W$
- Area under isotherm:

$$\int_{P_1}^{P_2} PdV = \int_{V_1}^{V_2} RT_h \frac{dV}{V} = RT_h \log \frac{V_2}{V_1}$$

- Area under isobar:

$$P_2(V_2-V_1)=R(T_h-T_c)$$

- Subtract to find net work done and net heat exchange

Engine Cycles - Efficiency
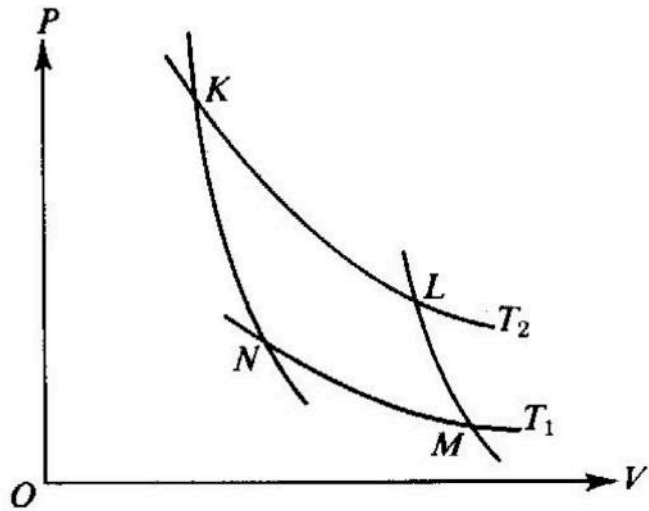
- Engine efficiency = (work done by the system during one cycle)/(heat extracted from the hot reservoir)
  - $e = W_{cycle}/|Q_H|$
  - Carnot cycle: $e_{Carnot} = 1 - T_C/T_H$
- Carnot cycle
  - Most efficient possible engine cycle
  - Zero entropy change

95. In the cycle shown above, KL and NM represent isotherms, while KN and LM represent reversible adiabats. A system is carried through the Carnot cycle $KLMN$, taking in heat Q_2 from the hot reservoir T_2 and releasing heat Q_1 to the cold reservoir T_1. All of the following statements are true EXCEPT:

(A) $Q_1/T_1 = Q_2/T_2$.
(B) The entropy of the hot reservoir decreases.
(C) The entropy of the system increases.
(D) The work W done is equal to the net heat absorbed, $Q_2 - Q_1$.
(E) The efficiency of the cycle is independent of the working substance.

16. An engine absorbs heat at a temperature of 727° C and exhausts heat at a temperature of 527° C. If the engine operates at maximum possible efficiency, for 2000 joules of heat input the amount of work the engine performs is most nearly

(A) 400 J
(B) 1450 J
(C) 1600 J
(D) 2000 J
(E) 2760 J

2nd Law of Thermodynamics

- Many ways to state:
  - Work must be done to transfer heat from a colder body to a hotter body
  - Heat energy <u>cannot</u> be converted into work with perfect efficiency
  - For any thermodynamic process, the net change in entropy must be greater than or equal to zero
  - Colloquially, "entropy always increases"

Oven   Lens   Sample
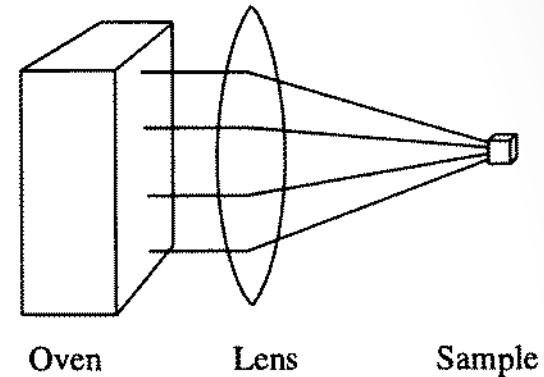
91. An experimenter needs to heat a small sample to 900 K, but the only available oven has a maximum temperature of 600 K. Could the experimenter heat the sample to 900 K by using a large lens to concentrate the radiation from the oven onto the sample, as shown above?

(A) Yes, if the volume of the oven is at least 3/2 the volume of the sample.
(B) Yes, if the area of the front of the oven is at least 3/2 the area of the front of the sample.
(C) Yes, if the sample is placed at the focal point of the lens.
(D) No, because it would violate conservation of energy.
(E) No, because it would violate the second law of thermodynamics.

3rd Law of Thermodynamics

- Cannot cool system to 0 K in a finite number of steps
- Nernst's Theorem:
  - At 0 temperature, any system's entropy is 0. We take this to be a universal constant.
  - (Experimentally verified as well)

$$\lim_{T \to 0} S(\vec{X}, T) = 0$$

Free Expansion of Ideal Gas

- N molecules of an ideal gas all occupy the left half of a thermally insulated box, while the right half is empty
- We remove the barrier and allow the gas to fill the whole box
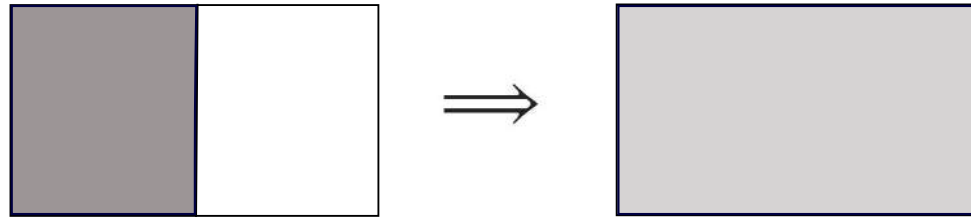
- What happens to the gas's temperature?
  - Stays constant
  - Microscopically, no change in kinetic energy of the gas molecules
  - Macroscopically, $U = U(T)$ for ideal gas, and U does not change
- What happens to the gas's entropy?
  - Increases
  - Free expansion is a spontaneous and irreversible process
  - Entropy is extensive

Van der Waals Gas

- Real gas molecules locally repel one another
- Van der Waals proposed new model that accounted for excluded volume of molecules
- New parameters:
  - a: intermolecular attraction
  - b: excluded volume
- Less accurate at lower T
  - Predicts *negative* dV/dP

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

79. Consider 1 mole of a real gas that obeys the van der Waals equation of state shown above. If the gas undergoes an isothermal expansion at temperature T_0 from volume V_1 to volume V_2, which of the following gives the work done by the gas?

(A) 0

(B) $RT_0 \ln\left(\dfrac{V_2}{V_1}\right)$

(C) $RT_0 \ln\left(\dfrac{V_2 - b}{V_1 - b}\right)$

(D) $RT_0 \ln\left(\dfrac{V_2 - b}{V_1 - b}\right) + a\left(\dfrac{1}{V_2} - \dfrac{1}{V_1}\right)$

(E) $RT_0\left(\dfrac{1}{(V_2 - b)^2} - \dfrac{1}{(V_1 - b)^2}\right) + a\left(\dfrac{1}{V_2^3} - \dfrac{1}{V_1^3}\right)$

Phase Transitions

- A qualitative change in the properties of matter
  - Liquid-solid, gas-liquid, paramagnet-ferromagnet
- (More abstractly, change in system symmetries)
- Example below
  - Phase diagram for liquid-gas transition in VDW gas
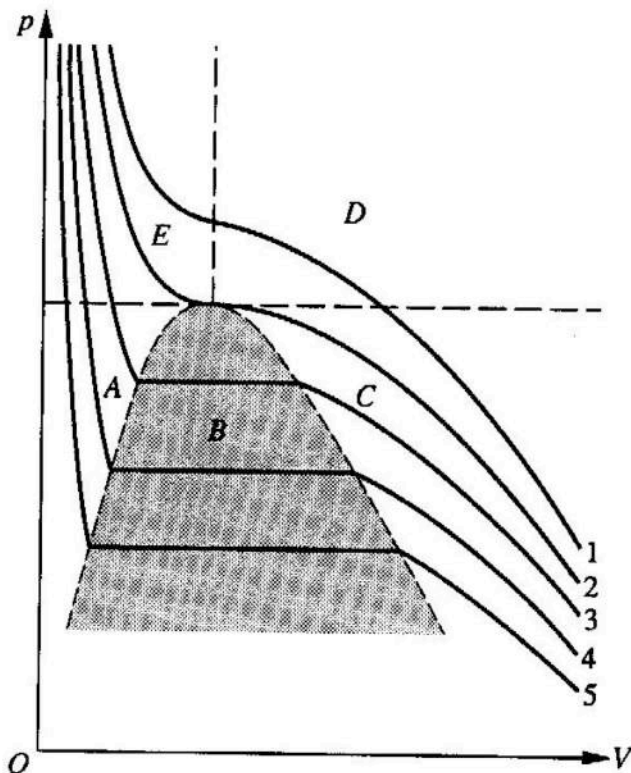
Isotherms and coexistence curves are shown in the pV diagram above for a liquid-gas system. The dashed lines are the boundaries of the labeled regions.

46. Which numbered curve is the critical isotherm?

  (A) 1
  (B) 2
  (C) 3
  (D) 4
  (E) 5

47. In which region are the liquid and the vapor in equilibrium with each other?

  (A) A
  (B) B
  (C) C
  (D) D
  (E) E

Phase Transitions

- Some phase transitions are characterized by divergences in measurable properties

- 1st order transition:
  - Sudden discontinuous change in system properties

- 2nd order transition:
  - Continuous change in system properties
  - Discontinuity in derivative

95. Which of the following curves is characteristic of the specific heat C_v of a metal such as lead, tin, or aluminum in the temperature region where it becomes superconducting?

(A)

(B)

(C)

(D)

(E)
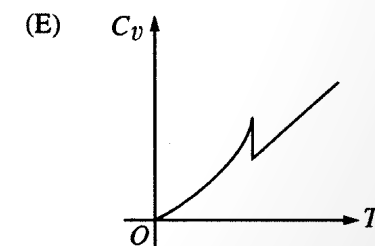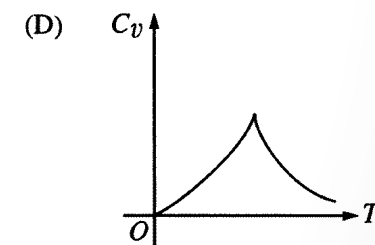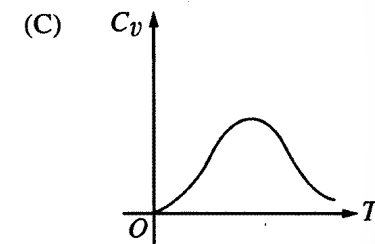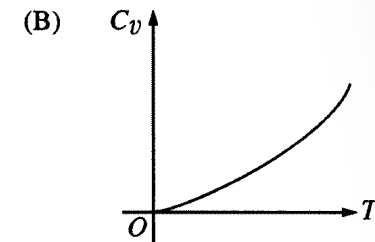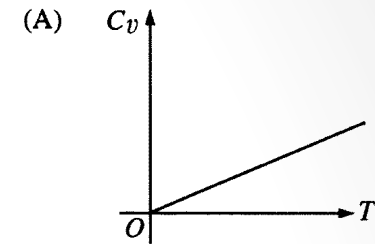
Thermodynamics Summary

- 1st Law of Thermodynamics
  - Manipulating Differentials
  - Ideal Gas Processes
  - Engine Cycles
- 2nd Law of Thermodynamics
  - Entropy
- Additional Topics
  - **Thermodynamic potentials** – Gibbs, Enthalpy, Helmholtz
  - Engine efficiency
  - 3rd Law of Thermodynamics
  - Van der Waals Gas
  - Phase Transitions