

# Department of Physics

## Preliminary Exam January 5–9, 2004

Day 4: Thermodynamics and Statistical Physics

Friday, January 9, 2004

9:00 a.m. – 12:00 p.m.

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### Instructions:

1. Write the answer to each question on a separate sheet of paper. If more than one sheet is required, staple all the pages corresponding to a *single* question together in the correct order. But, do *not* staple all problems together. This exam has *five* questions.
2. Be sure to write your exam identification number (*not* your name or student ID number!) and the problem number on each problem sheet.
3. The time allowed for this exam is three hours. All questions carry the same amount of credit. Manage your time carefully.
4. If a question has more than one part, it may not be necessary to successfully complete one part in order to do the other parts.
5. The exam will be evaluated, in part, by such things as the clarity and organization of your responses. It is a good idea to use short written explanatory statements between the lines of a derivation, for example. Be sure to substantiate any answer by calculations or arguments as appropriate. Be concise, explicit, and complete.
6. The use of electronic calculators is permitted. However, obtaining preprogrammed information from programmable calculators or using any other reference material is strictly prohibited. Oklahoma State University Policies and Procedures on Academic Dishonesty and Academic Misconduct will be followed.

## Useful Information

- **Physical constants and conversion factors:**

$$\begin{array}{lll} a_0 = 0.529 \text{ \AA} & e = 1.60 \times 10^{-19} \text{ C} & \hbar = 1.05 \times 10^{-34} \text{ J}\cdot\text{s} \\ k = 1.38 \times 10^{-23} \text{ J/K} & m_e = 9.11 \times 10^{-31} \text{ kg} & m_p = 1.67 \times 10^{-27} \text{ kg} \\ N_A = 6.02 \times 10^{23} \text{ mol}^{-1} & R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1} & \sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \\ 1 \text{ liter}\cdot\text{atm} = 101 \text{ J} & 1 \text{ cal} = 4.18 \text{ J} & 1 \text{ BTU} = 1.06 \text{ kJ} \end{array}$$

- **Temperature conversions:**

$$\text{Celsius to absolute (Kelvin):} \quad T_C = T_K - 273.15$$

$$\text{Fahrenheit to absolute (Rankine):} \quad T_F = T_R - 459.67$$

$$\text{Celsius to Fahrenheit:} \quad T_F = \frac{9}{5}T_C + 32 \quad (\text{exact})$$

- **Useful integrals and mathematical relations:**

$$\text{Gamma function:} \quad \Gamma(p+1) \equiv \int_0^\infty dz z^p e^{-z}$$

$$\Gamma(p+1) = p\Gamma(p)$$

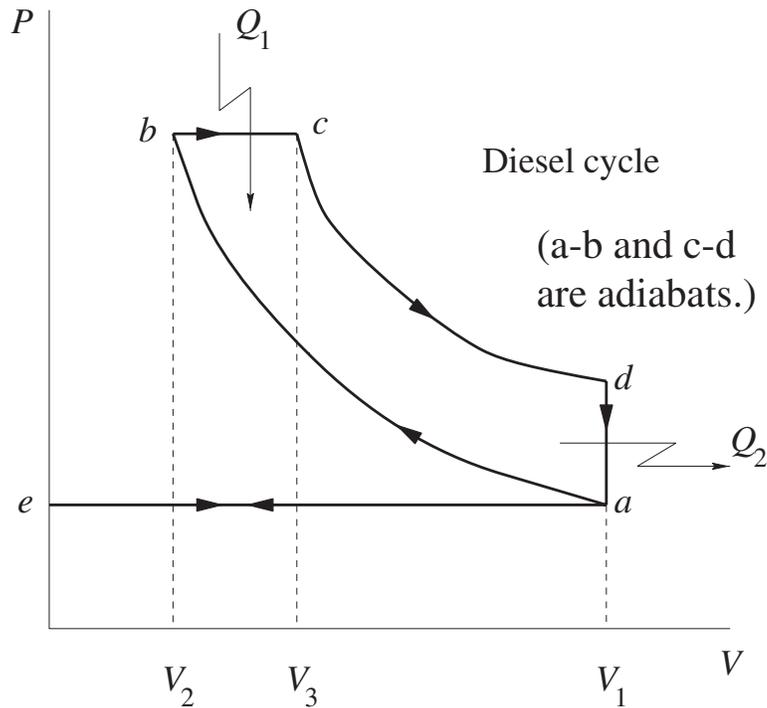
$$\Gamma(n) = (n-1)! \quad (\text{for } n \text{ a positive integer})$$

$$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$$

$$\text{Stirling's Approximation:} \quad \ln n! \sim n \ln n - n \quad (\text{for } n \gg 1)$$

### Problem 1

For the *Diesel cycle* shown in the figure, assume 1 lb of air to behave as an ideal gas, where ( $c_P = 0.238 \text{ BTU/lb} \cdot ^\circ\text{F}$ ,  $c_V = 0.170 \text{ BTU/lb} \cdot ^\circ\text{F}$ ),  $T_a = 100^\circ\text{F}$ ,  $T_c = 2400^\circ\text{F}$ ,  $P_a = 15 \text{ lb/in}^2$ , and  $P_b = P_c = 550 \text{ lb/in}^2$ .



Calculate:

- the heat added;
- the head rejected;
- the efficiency of the cycle.

[Note: See p. 2 for conversion formula between *Fahrenheit* and absolute (*Rankine*) temperature scales.]

## Problem 2

Suppose you have just made a hot cup of coffee, but you have still got 5 minutes until class. If you wish to bring your coffee to class as hot as possible, should you put the cream in now or just before class? When should you add the sugar? When should you stir it and for how long? If you don't want to stir it, should you leave the spoon in? Does it matter whether the spoon is plastic or metal? Would your answer be different if the cream were black instead of white? Does your answer depend on the color of your cup? Make numbers for your arguments if you can. (Flying Circus 3.91)

*Please give a written assessment of these questions, discussing what is important and not, including rough, order-of-magnitude estimations.*

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## Problem 3

Consider a very simple model of rubber in which we represent the system as a one-dimensional chain of  $N$  links each of length  $a$ , where  $N \gg 1$ . Each link is equally likely to be directed to the right or to the left of its connection with the adjoining link. In this model, the internal energy may be regarded as a function of temperature only.

- (a) For a given length  $x$ , calculate the number of possible configurations as a function of  $N$ ,  $a$ , and  $x$  ( $Na \gg x$ ).
- (b) Calculate the entropy in the limit where  $x \ll Na$  using Stirling's approximation.\*
- (c) Using the expression for the tension  $F = -T \left( \frac{\partial S}{\partial x} \right)_T$ , derive Hooke's law (for  $x \ll Na$ ).
- (d) Explain in your own words the origin of this force. (U. of Colorado prelim 1972.)

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\* See p. 2 for formula.

#### Problem 4

One (1) mole of a monatomic ideal gas at temperature  $T_1 = 250\text{ K}$  and pressure  $P$  is in one compartment of an insulated container. In an adjoining compartment separated by an insulating partition are two (2) moles of another monatomic gas at temperature  $T_2 = 340\text{ K}$  and pressure  $P$ . When the partition is removed:

- Calculate the final temperature ( $T_f$ ) of the mixture.
- Calculate the entropy change when the gases are *identical*.
- Calculate the entropy change when the gases are *different*.

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#### Problem 5

Consider a monatomic ideal gas in equilibrium with the surface of a solid. Some of the molecules of the gas will be adsorbed onto the surface, and the number adsorbed will depend upon temperature as well as the pressure of the gas. A simple statistical mechanical model for this system is to picture the solid surface to be a two-dimensional lattice of  $M$  sites. Each of these sites can be either unoccupied, or occupied by at most one of the molecules of the gas. Let the partition function of an unoccupied site be equal to 1 and that of an occupied site be equal to  $q(T)$ . [We do not need to know the precise functional form of  $q(T)$  here though for intuitive purposes think of a Boltzmann factor.] Assuming that molecules adsorbed onto the lattice sites do not interact with each other, the canonical partition function of  $N$  molecules adsorbed onto  $M$  sites is then

$$Q_{\text{ad}}(N, M, T) = \frac{M!}{N!(M-N)!} [q(T)]^N.$$

- First, *derive* the canonical partition function of a monatomic ideal gas of  $N'$  molecules (mass  $m$ ) in a volume  $V'$  at temperature  $T'$  as if the adsorbing surface were not present.  
(Answer:

$$Q_{\text{gas}} = \frac{1}{N'!} \left( \frac{V'}{\Lambda^3} \right)^{N'},$$

where

$$\Lambda = \Lambda(T') \equiv h/\sqrt{2\pi mkT'}$$

is sometimes called the *thermal wavelength* and has units of length.)

- (b) Now, using the fact that the adsorbed molecules are in equilibrium thermodynamically with the gas-phase molecules, derive an expression for the fractional coverage,  $\theta \equiv N/M$ , as a function of the temperature and pressure of the gas.

Answer:

$$\theta = \theta(T, P) = \frac{P}{P + \hat{P}(T)},$$

where

$$\hat{P}(T) \equiv \frac{kT}{\Lambda^3 q(T)}$$

HINT: At equilibrium, the *chemical potentials* must be equal for the two subsystems (i.e. *gas* and *adsorbate*). Same for the temperatures. Use Stirling's approximation\* to simplify all factorial expressions.

- (c) So, what will happen to  $\theta$ , the fraction of surface sites filled, in the appropriate (i) **low temperature** and (ii) **high temperature** limits? Interpret physically.

[For Part (c), assume  $q(T) = \exp(+|\varepsilon|/kT)$ , meaning that each site is a potential *well*.]

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\* See p. 2 for formula.