First Examination KEY
Feb 1, 2008
No Calculators, please put them away.
Useful information and equations:

Law IA: $\Delta U = q + w$
Law IB:

$H = U + PV$
Heat Capacity
$C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$C_P = \left(\frac{\partial H}{\partial T}\right)_P$

Work:
$w = -P_{ext}dV$
$w = mgh$
$g = 10 \text{ m/sec}^2$
$w = IQt$

Kinetic Energy: $\varepsilon = \frac{mv^2}{2}$

Isothermal Reversible work:
$w = -nRT\ln\left(\frac{V_f}{V_i}\right)$
$PV = Const$

Adiabatic Reversible work: $w = -PdV$
$P\left(V^{\gamma}\right) = Const;\quad \text{where } \gamma = \frac{C_{P,m}}{C_{V,m}}$

Thermodynamic Equations of State
$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$

Thermal expansion and compression coefficient
$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

$\kappa = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

IG EoS (and other IG relations)
$PV_m = RT$
$C_{P,m} = C_{V,m} + R$
$\Delta U = C_V \Delta T$
$\Delta H = C_P \Delta T$

vdW EoS
$P = \frac{RT}{V_m - b} - \frac{a}{V_m^{\ 2}}$
$U = U(T,V)$
$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

Cyclic rule:
$\left(\frac{dx}{dy}\right)_z \left(\frac{dz}{dx}\right)_y \left(\frac{dy}{dz}\right)_x = -1$

Calculus Rules:
$\frac{d(yz)}{dx} = z\frac{d(y)}{dx} + y\frac{d(z)}{dx}$

$\frac{dx}{dz} = \frac{dy}{dz}\frac{dx}{dy}$

$\Delta Z = \int_{x_i}^{x_f}\left(\frac{\partial Z}{\partial x}\right)_y dx$

Gas Constant:
$R = 8J/mol - K$
$R = 0.08L - atm/mol - K$
$R \cdot 300K = 2.5kJ/mol$
$1Atm \approx 1bar = 10^5 Pa$
$T(K) = T(C) + 273$

Show your work throughout, always write down the equations you are using before substituting in numerical values and always show units for computed quantities. You do not need to compute the final number if you do not want to but show where the numbers you are given can be used.

Name __________KEY____________________

ID__________________

This page is left blank. Use it for extra work if you need it. Please leave it attached to the rest of the exam.

1. Human being expend energy during expansions and contraction of their lungs breathing. Each exhalation from the lungs of an adult involves pushing out about 0.5 L of gas against 1 Atm of pressure. This occurs about 15,000 times in a 24 hr day. (Remember the answer is only needed to one sig fig, which means just get the exponent correct to get an order of magnitude answer.)

a. **(6pts)** Estimate the amount of work in breathing done by each person in the course of a 24 hr day. Write down the equations you use to compute this before substituting in.

$$w_B = -P\Delta V = -1Atm \cdot \frac{1}{2} l \left(\frac{100J}{1L \cdot atm}\right) = -50 \,{}^{J}\!/_{breath}$$

$$w = w_B \frac{3}{2} \cdot 10^4 = -750 \,{}^{kJ}\!/_{day}$$

b. **(6pts)** As a comparison, estimate the work done to raise a 10 kg mass 100 m (which is about a 30 story building)

$$w = mgh = 10kg \cdot 10m/s^2 \cdot 100m \cdot \left(\frac{1kJ}{1000J}\right) = 10kJ$$

2) Your lungs also lose heat because our body is at $37°C$ and the air (for purposes of this question) is at $17°C$. The heat capacity of air is around $C_{m,p} = \frac{7}{2}R = 30 \,{}^{J}\!/_{(mol-K)}$. As in problem 1, assume the breathing is at constant pressure (1 Atm).

a. **(6pts)** Estimate the change in enthalpy of the air in a 0.5 L breath for this process.

$$n = \frac{0.5L}{22.4L/mol} = \frac{1}{40} moles$$

$$\Delta H_{Breath} = C_P \Delta T = n \cdot C_{m,P} \Delta T = \frac{1}{40} \cdot 30J/molK \cdot 20K = 15 \,{}^{J}\!/_{Breath}$$

b. **(6pts)** Assuming we take 15,000 breaths per day, how much heat is lost (to the environment) each day, by just breathing?

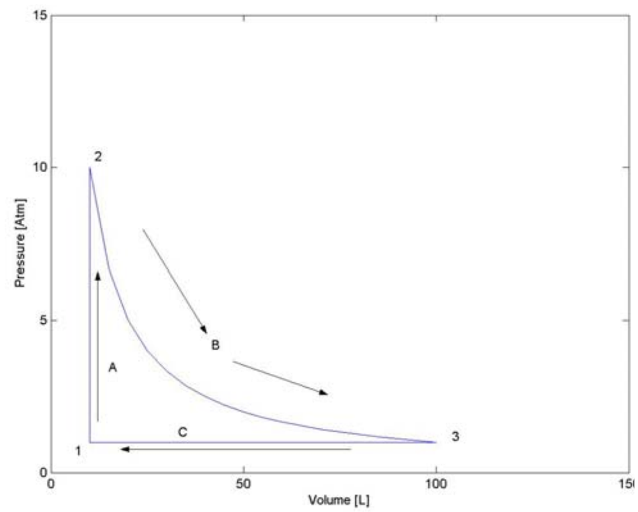
$$q_P = N \cdot \Delta H_{Breath} = \left(1.5 \cdot 10^4 \,{}^{breaths}\!/_{day}\right) 15 \,{}^{J}\!/_{breath} \left(1kJ \,/_{1000J}\right) = 200 \,{}^{kJ}\!/_{day}$$

3. Consider a gas undergoing a cyclic process. An ideal gas described by an initial state of $T_I = 300K$, $P_I = 1\ Atm$, and $V_I = 10\ l$, is heated in the first step (process A) at constant volume until the pressure is $10\ Atm$. In the second step (B) it undergoes reversible isothermal expansion until the pressure is back to $1\ Atm$. In the third step (C) it is restored to its original state by the extraction of heat at constant pressure. Assume $C_{m,V} = \frac{5}{2}R = 20\ J/(mol-K)$. Label the states 1, 2 and 3, and the steps of the process by A, B and C.

c. **(10pts)** Fill in the table for P, V and T for the three states

State	1	2	3
P(Atm)	1	10	1
V(liters)	10	10	$V_3 = \frac{P_2}{P_3}V_2 = 10 \cdot 10 = 100$
T(K)	300	$T_2 = \frac{P_2}{P_1}T_1 = 3000$	3000

d. **(8pts)** Draw a P-V diagram of this process, labeling the states 1, 2 and 3, and the steps of the process by A, B and C.



c. **(12pts)** Compute the work done on each step of the process, Label the work w_A w_B and w_C.

$\log_e(10) = 2.3$

$$n = \frac{PV}{RT} = \frac{10^5 Pa \cdot 10^{-2} m^3}{8J/molK \cdot 300K} = \frac{1}{2.5} = 0.5mol$$

$$w_A = -PdV = 0J$$

$$w_B = -\int PdV = -nRT\ln\left(\frac{V_3}{V_2}\right) = -\frac{25}{2.5}\ln(10) = -23kJ$$

$$w_C = -P_x\Delta V = -1bar \cdot (V_1 - V_3) \cdot 10^2 \frac{J}{L \cdot atm} = -1 \cdot (10-100) \cdot 10^2 \frac{J}{L \cdot atm} \cdot (\frac{1kJ}{1000J}) = 10kJ$$

4a) **(10pts)** Derive the dependence of the constant volume heat capacity, C_V, on volume. Show that

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

Assume that U is a state function, and an exact differential, that depends on T and V: $U = U(T,V)$.

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad and \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial\left(\frac{\partial U}{\partial T}\right)_V}{\partial V}\right)_T = \left(\frac{\partial\left(\frac{\partial U}{\partial V}\right)_T}{\partial T}\right)_V = \left(\frac{\partial\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]}{\partial T}\right)_V$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial T}\right)_V + T\left(\frac{\partial\left(\frac{\partial P}{\partial T}\right)_V}{\partial T}\right)_V - \left(\frac{\partial P}{\partial T}\right)_V = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

4b) **(10pts)** Use the above expression and determine the dependence of the heat capacity on the volume for the van der Waals gas. (Evaluate the derivative $\left(\frac{\partial C_V}{\partial V}\right)_T$ for the van der Waals gas.)

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial\left[\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right]}{\partial T}\right)_V = \frac{R}{V_m - b}$$

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V = \left(\frac{\partial\left[\frac{R}{V_m - b}\right]}{\partial T}\right)_V = 0$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0$$

5a) **(8pts)** In general the constant pressure, C_P , and constant volume, C_V, heat capacities of any substance are related by: $C_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$

Evaluate the difference, $C_P - C_V$, for the ideal gas.

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = T\left(\frac{P}{T}\right)\left(\frac{V}{T}\right) = \frac{nRT}{T} = nR$$

5b) **(12pts)** Assume that one mole of an ideal gas, with a heat capacity, $C_V = 30 \, {}^{J}\!/_{mole-K}$, expands under constant pressure, so that the temperature is <u>increased</u> by 200 degrees Kelvin. The pressure is not given, nor is the volume. (You may use the relation of part 5a). Set up the appropriate equations and solve for q, w, ΔU, and ΔH . You do not need to compute the final number if you do not want to but show where the numbers you are given can be used.

$$q = q_P = \Delta H = C_p \Delta T = (C_V + nR)\Delta T = 38\frac{J}{K}\cdot 200\left(\frac{1kJ}{1000J}\right) = 8kJ$$

$$\Delta U = C_V \Delta T = 30\frac{J}{K}\cdot 200K\left(\frac{1kJ}{1000J}\right) = 6kJ$$

$$\Delta U = q + w = C_p \Delta T + w = C_V \Delta T$$

$$w = C_V \Delta T - C_p \Delta T = -nR\Delta T = -8\frac{J}{K}\cdot 200K\left(\frac{1kJ}{1000J}\right) = -1.6kJ$$

5c) **(6pts)** Note what the sign of the work is and explain the sign in terms of the process.

The sign of the work is negative. Because the gas expands, the volume change is positive and the external pressure is a constant. If the work could have been computed from that information, because $w = -P_x \Delta V$, the work would have been negative, indicating that the system did work on the surroundings (or transferred work to the surroundings).

Exam Statistics:

Mean: 77
Standard Deviation: 17
Median: 81
High: 99 (out of 100 possible points)