1. (25 Points) ***Do 5 out of 6*** (If 6 are done only the first 5 will be graded)***

a). Define the terms: open system, closed system and isolated system in terms of flows between a system and its surroundings.

Open: matter can transfer between system and surroundings.
Closed: matter cannot transfer between system and surroundings.
Isolated: no transfer of anything between system and surroundings.

b). Classify the energy and the square of the pressure as intensive, extensive or neither: Explain your reasoning.

Energy is intensive since it is proportional to the number of atoms in the material. The pressure is independent of the system size so it is intensive. Taking its square does not change this feature.

c). What is the condition for thermal equilibrium between ten thousand systems?

The temperatures of all ten thousand systems must have the same value.
d). Define mathematically the relationship between an *exact differential* and a *state function* with two independent variables.

In order for a function $f(x,y)$ to be a state function, it must be possible to write the total differential $df$ in the form $df = \left( \frac{\partial f}{\partial x} \right)_y \, dx + \left( \frac{\partial f}{\partial y} \right)_x \, dy$. If the form $df$ as written exists, it is an exact differential.

e). Two ideal gas systems undergo reversible expansions starting from the same $P$ and $V$. At the end of the expansions, the two systems have the same volume. The pressure in the system that has undergone an adiabatic expansion is lower than that in the system that has undergone an isothermal expansion. Explain this result *without* using equations.

In the system undergoing adiabatic expansion, all the work done must come through the lowering of $\Delta U$, and therefore of the temperature. By contrast, some of the work done in the isothermal expansion can come at the expense of the heat that has flowed across the boundary between the system and surroundings.

f). What is wrong with the following statement (that often appears in newspapers)?: “Because the well insulated house stored a lot of heat, the temperature didn't fall much when the furnace failed”.

Rewrite the sentence to convey the same information in a correct way.

Heat cannot be stored – it is not a state function. Something like the following is safe. “Because the house was well insulated, the walls were nearly adiabatic. Therefore, the temperature of the house did not fall as rapidly when in contact with the surroundings at a lower temperature as would have been the case if the walls were diathermal”.

2. (26 points)

The internal energy $U$ is a function of the independent variables $T$ and $V$, $U = f(T, V)$.

As a consequence, $dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV$. The enthalpy $H = U + PV$.

A. Develop (all details shown) an expression for $\left( \frac{\partial U}{\partial T} \right)_P$.

Considering $P$ fixed and dividing by $dT$ for fixed $P$ yields, since $\left( \frac{\partial T}{\partial T} \right)_p = 1$,

$$\left( \frac{\partial U}{\partial T} \right)_p = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p$$

B. Using A and the definition of the heat capacities $C_V = \left( \frac{\partial U}{\partial T} \right)_V$ and $C_p = \left( \frac{\partial H}{\partial T} \right)_p$ develop an expression for $C_p - C_V$.

$$C_p - C_V = \left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial (U + PV)}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_V$$

$$= \left( \frac{\partial U}{\partial T} \right)_p + P \left( \frac{\partial V}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_V$$

Substitute in from A to get

$$C_p - C_V = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p + P \left( \frac{\partial V}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_V$$

$$= \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p + P \left( \frac{\partial V}{\partial T} \right)_p \left[ \left( \frac{\partial U}{\partial T} \right)_V + P \left( \frac{\partial V}{\partial T} \right)_p \right]$$
3. (25 points) For ammonia measurement gives \( \left( \frac{\partial U}{\partial V} \right)_T = 840 \text{ J/m}^3 \text{ mole} \) at 300 K and 
\( \left( \frac{\partial U}{\partial T} \right)_V = 37.3 \text{ J/K mole} \).

Estimate the change in molar energy of ammonia when it is heated through 2 K and compressed through 100 cm\(^3\).

(Hint. Use the general expression for \( dU \) in question 2 and replace differentials by small but finite changes).

From \( dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \) and assuming over small \( T \) and \( V \) ranges that the 
coefficients are constants, then

\[
\Delta U = \left( \frac{\partial U}{\partial T} \right)_V \Delta T + \left( \frac{\partial U}{\partial V} \right)_T \Delta V.
\]

Plugging in the data, and noting that in a compression \( \Delta V < 0 \) and for heating \( \Delta T > 0 \):

\[
\Delta U = (37.3 \text{ J/K mole})(2 \text{ K}) + (840 \text{ J/m}^3 \text{ mole}) \left( -10^2 \text{ cm}^3 \left( \text{ m}/100 \text{ cm} \right)^3 \right)
\]

= 74.52 J/mole
4. (24 points)
For the following processes explain whether each of the quantities $q$, $w$, $\Delta U$ and $\Delta H$ is positive, zero, negative or ambiguous.

a) Reversible adiabatic expansion of an ideal gas.

$q=0$ since adiabatic.

$w$ negative for an expansion since $w = -\int pdV$ and $dV$ is positive for expansion.

Since $\Delta U = q + w$ $\Delta U$ is negative.

$\Delta H = \Delta U + \Delta (PV) = \Delta U + nR\Delta T$, for ideal gas. Also, $dU = C_v dT$. Since $dU < 0$ and $C_v > 0$ then $dT < 0$ and $\Delta T$ is negative. Therefore, with $\Delta U$ negative, $\Delta H$ is negative.

b) Reversible heating of a gas at constant pressure, $p$.

$q$ is positive since the gas is heated.

From the heat capacity definition, $dq_p = C_v dT$, and $C_v > 0$; so $dT > 0$. Then $\Delta T > 0$. From $dU = C_v dT$ and $C_v > 0$ $\Delta U$ is positive.

The ideal gas equation of state $pV = nRT$ and the fact that $\Delta T > 0$ then gives $\Delta V > 0$. Then, since $p$ is fixed, $w = -p\Delta V$ is negative.

From $\Delta H = \Delta U + \Delta (PV) = \Delta U + nR\Delta T$ and $\Delta U$ and $\Delta T$ are positive; $\Delta H$ is positive.

Or, $\Delta H = \Delta U + \Delta (PV) = \Delta U + p\Delta V$ and $\Delta U$ and $p\Delta V$ are positive, so $\Delta H$ is positive.
Mathematical expressions:
\[ \int x^a \, dx = x^{a+1} / (a+1); \quad n = 0, 1, 2, \ldots \]
\[ \int x^{-a} \, dx = \ln x \]
\[ \int x^{-a} \, dx = -x^{-(a-1)} / (a-1); \quad n = 2, 3, \ldots \]

Euler: \( \frac{\partial x}{\partial y} \frac{\partial y}{\partial z} \frac{\partial z}{\partial x} \) = -1

Inverter: \( \frac{\partial x}{\partial y} \frac{\partial y}{\partial z} \frac{\partial z}{\partial x} \) = \( \int \frac{\partial x}{\partial y} \)

\[ dU = \delta q + \delta w \]
\[ \delta w = -Pe_{ext}dV \]
\[ dU = C_VdT \]
\[ \Delta U = q_v \]
\[ C_V = (\partial U / \partial T)_V \]
\[ H = U + PV \]
\[ \Delta H = q_p \]
\[ C_P = (\partial H / \partial T)_P \]

\[ \mu_{VT} = (\partial T / \partial P)_H = - (\partial H / \partial P)_T / C_P \]

\[ \mu_{VT} = H(T_2) = H(T_1) + \int_{T_1}^{T_2} (C_P) dT \]

\[ dS = \delta q_{rev} / T \]
\[ \Delta S_{univ} = \Delta S + \Delta S_{surr} \]

\[ S = k_B \ln W \]

\[ S = U / T + k_B \ln Q \]

\[ S(T_2) = S(T_1) + \int_{T_1}^{T_2} (C_v / T) dT \]

\[ dH = dU + d(PV) \]
\[ dU = Tds - Pdv \]
\[ dH = Tds + Vdp \]

\[ A = U - TS \]
\[ dA = dU - T ds \]
\[ dA = -Pdv - SdT \]

\[ G = H - TS \]
\[ dG = dH - Tds \]
\[ dG = Vdp - SdT \]

\[ (\partial U / \partial S)_V = T \]
\[ (\partial U / \partial V)_S = -P \]
\[ (\partial U / \partial T)_P = -S \]

\[ (\partial H / \partial S)_P = T \]
\[ (\partial H / \partial P)_S = V \]
\[ (\partial H / \partial T)_V = -S \]

\[ (\partial A / \partial V)_T = -P \]
\[ (\partial A / \partial T)_V = -S \]

\[ (\partial G / \partial T)_P = -S \]
\[ (\partial G / \partial P)_T = V \]
\( \frac{\partial U}{\partial V} = T \left( \frac{\partial P}{\partial T} \right)_V - P \)

\[ A = \kappa R \ln Q \]

\( C_p - C_v = \alpha \nu R \)

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

\( \alpha = \left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial T} \right)_P \)

\[ V = v_0 \exp(-\kappa P) \exp(\alpha T) \]

\( \Delta G(V_1 \rightarrow V_2, \text{isothermal}) = \int_{P_1}^{P_2} V dP \)

\( \Delta r G(T_1 \rightarrow T_2, \text{isobaric}) = \int_{T_1}^{T_2} -SdT \)

\( \Delta r H = \Delta r H^0 + \int_{298}^{T} \left( \frac{\partial \Delta r H}{\partial T} \right)_P dT \)

\( \Delta r S = \Delta r S^0 + \int_{298}^{T} \left( \frac{\Delta C_p}{\partial T} \right)_T dT \)

\[ \sum_i \eta_i \delta \mu_i + SdT - VdP = 0 \quad \text{(Gibbs-Duhem)} \]

\[ \sum_i V_i \mu_i = 0 \quad \text{(reaction equilibrium)} \]

\[ \mu_i = \mu_i^0 + RT \ln a_i; \quad a_i = \gamma_i x_i; \]

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<th>Unit</th>
<th>Value</th>
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<tr>
<td>Gas constant</td>
<td>( R )</td>
<td>8.3145 J mol(^{-1}) K(^{-1})</td>
<td>8.3145 \times 10(^7) erg mol(^{-1}) K(^{-1})</td>
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<td>8.3145 m(^3) Pa mol(^{-1}) K(^{-1})</td>
<td>83.145 cm(^3) bar mol(^{-1}) K(^{-1})</td>
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<td>82.057 cm(^3) atm mol(^{-1}) K(^{-1})</td>
<td>1.9872 cal mol(^{-1}) K(^{-1})</td>
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<td>Avogadro constant</td>
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<tr>
<td>Faraday constant</td>
<td>( F )</td>
<td>96485.34 C mol(^{-1})</td>
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<tr>
<td>Speed of light in vacuum</td>
<td>( c )</td>
<td>2.99792458 \times 10(^8) m s(^{-1})</td>
<td>2.99792458 \times 10(^{10}) cm s(^{-1})</td>
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<tr>
<td>Planck constant</td>
<td>( h )</td>
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<td>6.62607 \times 10(^{-27}) erg s</td>
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