## Chemistry 342

## First Exam

## February 4, 2005

## 2:00 PM in C6 Lecture Center

Write all work you want graded in the spaces provided. Both the logical solution to the problem and the answer to the question are required. Final numerical values receive only small additional credit. What is required is an answer in terms of the original numerical data, including all numerical values and units of conversion factors. Use no intermediate calculated numbers, except where such numbers arise from answers to previous parts. The solution has to be worked out in the form of complete equations, with justification or basis for the use in the specific problem.
Example:

| Solutions |  |
| :---: | :---: |
| Step 1 | $\mathrm{d} w=-p_{o p} \mathrm{~d} V$ definition <br> $\mathrm{d} \boldsymbol{U}=C_{\mathrm{V}} \mathrm{d} T+(\partial \boldsymbol{U} / \partial V)_{T} \mathrm{~d} V$ <br> Apply $\mathrm{dV}=0$ (constant volume) $\begin{aligned} & \therefore w=0 \\ & \therefore \mathrm{~d} U=C_{\mathrm{V}} \mathrm{~d} T \end{aligned}$ <br> Apply $C_{V}=(3 / 2) R$ (given) <br> integrate to $\Delta \boldsymbol{U}=\int C_{V} \mathrm{~d} T=(3 / 2) \mathrm{R}\left[T f-T_{i}\right]$ <br> $\Delta \boldsymbol{U}=q+w$ First Law <br> Rearrange and apply $w=0$ $q=\Delta \boldsymbol{U}-0$ |
| Step 2 | $\mathrm{d} \boldsymbol{U}=C_{\mathrm{V}} \mathrm{~d} T+(\partial \boldsymbol{U} / \partial V)_{T} \mathrm{~d} V$ <br> Apply $\mathrm{d} T=0$ (constant temperature) <br> Apply $(\partial \mathbf{U} / \partial V)_{T}=0$ (ideal gas) $\begin{aligned} & \therefore \Delta \boldsymbol{U}=0+0 \\ & \mathrm{~d} w=-p_{\text {op }} \mathrm{d} V \text { definition } \\ & \text { Apply } p_{\text {op }}=p_{\text {gas }} \text { (reversible process) } \\ & p_{\text {gas }}=\mathrm{nRT} / V \text { (ideal gas) } \\ & \therefore w=-\int p_{\text {gas }} \mathrm{d} V=-\int \mathrm{nRT} / V \mathrm{~d} V=-\mathrm{nR} T \ln (V f / V i) \end{aligned}$ <br> $\Delta \boldsymbol{U}=q+w$ First Law <br> Rearrange and apply $\Delta \boldsymbol{U}=0$ and $w=-\mathrm{nR} T \ln (V f / V i)$ from above, $\therefore q=+\mathrm{nR} T \ln \left(V f / V_{i}\right)$ |


| Answers | Work, joules | Heat, joules |
| :--- | :--- | :--- |
| Step 1 | 0 J | $(3 / 2)(8.3144)(273-172)=1260 \mathrm{~J}$ |
| Step 2 | $-8.3144(273) \ln (1 / 2)=+1573 \mathrm{~J}$ | $8.3144(273) \ln (1 / 2)=-1573 \mathrm{~J}$ |

POSSIBLY USEFUL INFO: $\quad 1 \mathrm{~J}=1 \mathrm{~kg} \mathrm{~m}^{-2} \mathrm{~s}^{-2} \quad\left(p+\mathrm{n}^{2} \mathrm{a} / V^{2}\right)(V-\mathrm{nb})=\mathrm{nRT}$
$\mathrm{R}=8.31441 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}=1.98718 \mathrm{cal} \mathrm{mol}^{-1} \mathrm{~K}^{-1}=0.082057 \mathrm{~L} \mathrm{~atm} \mathrm{~mol}{ }^{-1} \mathrm{~K}^{-1} 1 \mathrm{~atm}=101325 \mathrm{~Pa}$
$(\partial \mathbf{U} / \partial V)_{T}=T(\partial p / \partial T)_{V}-p \quad(\partial H / \partial p)_{T}=-T(\partial V / \partial T)_{p}+V \quad \mu_{\mathrm{JT}} \equiv(\partial T / \partial p)_{H} \quad(\partial H / \partial p)_{T}=-C_{p} \mu_{\mathrm{JT}}$
$C_{p}-C_{V}=\left\{p+\left(\partial \mathbf{U} / \partial V_{T}\right\}(\partial V / \partial T)_{p}\right.$
special case : $\left.\left[T_{f} / T_{i}\right]^{C V / R}\right\}=\left[V_{i} / V_{f}\right]$ only for ideal gas undergoing reversible adiabatic process

1. Two moles of a van der Waals gas undergoes isothermal expansion from $1 \mathrm{~atm}, 200 \mathrm{~K}$ to ten times its initial volume against a constant pressure of 0.1 atm . The parameters for this gas are: $\mathrm{a}=1.4 \mathrm{~L}^{2} \mathrm{~atm} \mathrm{~mol}{ }^{-2}, \mathrm{~b}=0.39 \mathrm{~L} \mathrm{~mol}^{-1}$ $\mathrm{C}_{\mathrm{V}}=(5 / 2) \mathrm{R}-0.370 \times 10^{-3} \mathrm{~T}+25.46 \times 10^{-7} \mathrm{~T}^{2} \mathrm{cal} \mathrm{mol}{ }^{-1} \mathrm{~K}^{-1}$.
Find the initial volume in liters, final pressure in atm, $\boldsymbol{w}, \boldsymbol{q}, \Delta \boldsymbol{U}, \Delta \boldsymbol{H}$ in J
Space for a sketch (if desired)

| Solutions |  |
| :--- | :--- |
| initial volume |  |
|  |  |
| final pressure |  |
| $w$ |  |
| $q$ |  |


| $\Delta \boldsymbol{U}$ |  |  |
| :--- | :--- | :--- |
|  |  |  |
|  |  |  |
| $\Delta \boldsymbol{H}$ |  |  |


|  | Answers | Final number | Units |
| :--- | :--- | :--- | :--- |
| initial volume |  |  | L |
| final pressure |  |  | atm |
| $\boldsymbol{w}$ |  |  | J |
| $\boldsymbol{q}$ |  |  | J |
| $\Delta \boldsymbol{U}$ |  |  | J |
| $\Delta \boldsymbol{H}$ |  |  |  |

2. The compressibility factor for a gas at $20^{\circ} \mathrm{C}$ is described by this equation for pressures up to 10 atm:
$Z=1-2.024 \times 10^{-2} p$. The following properties of this gas are also known:
$C_{V}=2.97+10.5 \times 10^{-3} \mathrm{~T} \mathrm{cal} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$
$C_{p}=5.65+11.44 \times 10^{-3} T \mathrm{cal} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$
$(\partial \mathrm{U} / \partial \mathrm{V})_{\mathrm{T}}=2 \times 10^{-3} \mathrm{cal} \mathrm{L}^{-1}$
Two moles of a gas is compressed adiabatically in a single stage with a constant opposing pressure equal to 10 atm . Initially the gas is at $20^{\circ} \mathrm{C}$ and 1 atm pressure. The final pressure is 10 atm. Find the initial volume, final volume in liters, final temperature, $\boldsymbol{w}, \boldsymbol{q}, \Delta \boldsymbol{U}, \Delta \boldsymbol{H}$ in J

Space for a sketch (if desired)

| Solutions |  |
| :--- | :--- |
| initial volume |  |
| final volume |  |
|  |  |
| final <br> temperature |  |
|  |  |


| $\boldsymbol{w}$ |  |
| :--- | :--- |
| $\boldsymbol{q}$ |  |
| $\Delta \boldsymbol{U}$ |  |
| $\Delta \boldsymbol{H}$ |  |


|  | Answers | Final number | Units |
| :---: | :---: | :---: | :---: |
| initial volume |  |  | L |
| final volume |  |  |  |
| final temperature |  |  |  |
| $w$ |  |  |  |
| $q$ |  |  |  |
| $\Delta \boldsymbol{U}$ |  |  |  |
| $\Delta H$ |  |  |  |

3. When a system is taken from state $A$ to state $B$ along the path $A \rightarrow C \rightarrow B$ in the figure below, 80 J of heat flows into the system and the system does 30 J of work.


Volume, V
(a) How much heat flows into the system along the path $\mathrm{A} \rightarrow \mathrm{D} \rightarrow \mathrm{B}$ if the work done is 10 J ?
(b) When the system is returned from state $B$ to $A$ along the curved path, the work done on the system is 20 J . Does the system absorb or liberate heat, and how much?
(c) If $\boldsymbol{U}_{\mathrm{D}}-\boldsymbol{U}_{\mathrm{A}}=+40 \mathrm{~J}$, find the heat absorbed in each of the processes $A \rightarrow D$ and $\mathrm{D} \rightarrow \mathrm{B}$

|  | Solution | Numerical <br> Answer, J |
| :--- | :--- | :--- |
| (a) |  | $q_{\mathrm{A} \rightarrow \mathrm{D} \rightarrow \mathrm{B}}=$ |
| (b) |  | $q_{\mathrm{B}_{\mathrm{B}} \mathrm{A}}=$ |
| (c) |  | $q_{\mathrm{A} \rightarrow \mathrm{D}}=$ <br> $q_{\mathrm{D} \rightarrow \mathrm{B}}=$ |

4. A cylindrical container of fixed total volume is divided into three sections, $S_{1}, S_{2}$, and $S_{3}$. The sections $S_{1}$ and $S_{2}$ are separated by an adiabatic piston, whereas $S_{2}$ and $S_{3}$ are separated by a diathermic (heat conducting) piston. The pistons can slide along the walls of the cylinder without friction. Each section of the cylinder contains 1.00 mole of a perfect diatomic gas [ $\left.C_{V}=(5 / 2) R\right]$. Initially the gas pressure in all three sections is 1.00 atm and the temperature is 298 K . The gas in $S_{1}$ is heated slowly until the temperature of the gas in $S_{3}$ reaches 348 K . Find the final temperature, pressure, and volume, as well as the change in internal energy for each section. Determine the total energy supplied to the gas in $\mathrm{S}_{1}$.

Space for a sketch (required)

Solution:

| Final Numerical Answers |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Section $\mathrm{S}_{1}$ |  |  |  |  |
| $p_{\text {f1 }}=\quad$ atm | $p_{\text {t2 }}=$ | atm | $p_{\text {f3 }}=$ | atm |
| $V_{\text {f1 }}=1$ | $V_{\text {f2 }}=$ | L | $V_{f 3}=$ | L |
| $T_{f 1}=\quad \mathrm{K}$ | $T_{\text {f2 }}=$ | K | $T_{f 3}=$ | K |
| $\Delta \boldsymbol{U}_{1}=\quad \mathrm{cal}$ | $\frac{\Delta \boldsymbol{U}_{2}=}{\text { gas in Section } \mathrm{S}_{1}=}$ |  | $\Delta \boldsymbol{U}_{3}=$ | cal |
| Total energy supplied to the gas in Section $\mathrm{S}_{1}=$ |  |  | cal |  |

5.(a) The following data have been obtained for the density of a gas as a function of pressure at $10^{\circ} \mathrm{C}$. find the molar mass (molecular weight) of the gas.

| $\mathrm{p}, \mathrm{atm}$ | 0.68 | 2.72 | 8.14 |
| :--- | :--- | :--- | :--- |
| $\rho, \mathrm{~g} \mathrm{~L}^{-1}$ | 1.29 | 5.25 | 16.31 |

Hint: the gas is not ideal but you can find the limit of $\rho / p$ as the gas approaches ideality.

| p, atm | 0.68 | 2.72 | 8.14 |
| :--- | :--- | :--- | :--- |
| $\rho / \mathrm{p}, \mathrm{g} \mathrm{L}^{-1} \mathrm{~atm}^{-1}$ |  |  |  |

The graph (required):


| Solution | Answer | Final <br> number | Units |
| :--- | :--- | :--- | :--- |
|  |  |  | $\mathrm{g} \mathrm{mol}^{-1}$ |
|  |  |  |  |

5.(b) Given the $p \vee$ plots for a gas in the figure below:


|  | Numerical <br> Answer | ${ }^{\circ} \mathrm{C}$ |
| :--- | :--- | :--- |
| (a) What is the critical temperature of the gas? |  | ${ }^{\circ} \mathrm{C}$ |
| (b) What is the critical pressure of the gas? | $\mathrm{mol}^{2}$ |  |
| (c) A sample of the gas is collected in a flask at $325^{\circ} \mathrm{C}$. As it is <br> slowly cooled, it condenses at $250^{\circ} \mathrm{C}$. What is the density of the <br> sample? |  | $\mathrm{mol}^{-1}$ |
| (d) What is the vapor pressure in equilibrium with the liquid at <br> $275^{\circ} \mathrm{C}$ ? |  | atm |

(c) The critical temperature and pressure for several gases are shown below:

| gas | $T_{c}, \mathrm{~K}$ | $p_{c}, \mathrm{~atm}$ |
| :--- | :--- | :--- |
| A | 300 | 50 |
| B | 600 | 40 |
| C | 280 | 10 |
| D | 20 | 5 |

Consult the figure on the next page and answer these questions based on it

|  | Solution and Reasoning | Answer choose one |
| :---: | :---: | :---: |
| (a) Which gas is most nearly ideal in behavior at 300 K and 10 atm ? |  | ${ }^{A}{ }_{C}$ |
| (b) Which is the least ideal |  | $\begin{array}{ccc}A & & \\ & \\ & & \\ & & \\ & & \\ & \end{array}$ |



