

Name: _____
140 points
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Test 1
Chemistry 261
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**Answer the following multiple choice questions for 10 points each.
Must show complete work for full credit to be given:**

1. For an ideal gas, $Z = 1$ always whereas for a real gas A at low to moderate pressure, $Z < 1$. If the molar volume of an ideal gas is 22.4 L/mol at 1.0 atm pressure and 273 K, do you expect the volume for the real gas A under the same pressure and temperature to
- A) be the same B) be larger C) be smaller D) may not be calculated

$Z = p V_m / R T$. Assuming that p and T are fixed when comparing the ideal and the real gases, the change in Z must be a direct result of a change in V_m . $Z < 1$ indicates $V_m < V_{m,ideal}$. Answer is thus (C).

2. For an ideal gas, $C_v = 3 n R / 2$ and $C_p = 5 n R / 2$. What is the final volume if 2.00 L of an ideal gas at 500.0 K is adiabatically and reversibly cooled to 300.0 K?
- A) 4.68 L B) 2.72 L C) 2.81 L D) 4.30 L E) none of the above

$$V_f = V_i (T_i / T_f)^{c} = 2.00 \text{ L} (500.0 / 300.0)^{3/2} = 4.30 \text{ L} (D)$$

3. Calculate the work done when 5.00 mol of an ideal gas is expanded isothermally at 300.0 K from 5.00 atm to 2.00 atm pressure.
- A) -12.5 kJ B) 12.5 kJ C) -4.96 kJ D) 4.96 kJ E) none of the above

$$w = -n R T \ln (p_i / p_f) = -5.00 \text{ mol} \cdot 8.31451 \text{ J/mol K} \cdot 300.0 \text{ K} \cdot \ln (5.00 \text{ atm} / 2.00 \text{ atm}) = -11.5 \text{ kJ} (E)$$

Choose one of the following two exercises for 20 points:

4. A certain liquid has $\Delta_{\text{vap}} H^\circ = 32.0 \text{ kJ/mol}$. Calculate w , H , and U when 0.75 mol is vaporized at 260 K and 750 Torr.

$\Delta H^\circ = 0.75 \text{ mol} \cdot 32.0 \text{ kJ/mol} = +24.0 \text{ kJ}$ at 760 torr! At constant temperature, $dH = V dp$, thus to get ΔH at 750 torr, you need to consider $V \Delta p$. The liquid will have negligible volume relative to the gas. Thus the $V \Delta p = n R T \Delta p / p = 0.75 \text{ mol} \cdot 8.31451 \text{ J/mol K} \cdot 260 \text{ K} \cdot (-10 \text{ torr} / 750 \text{ torr}) = -21.6 \text{ J}$. This represents the enthalpy change of the product (the liquid reactant has no enthalpy change with pressure). Thus we should simply add this to the 24.0 kJ from the first step giving $\Delta H = 23.978 \text{ kJ}$. We should also consider the temperature change which would net a $dH = C_p dT$ change. Assuming the heat capacities are similar the net effect should be negligible. To get from ΔH to ΔU we need to subtract $\Delta(PV)$ which effectively is subtracting the gas portion only, since the liquid PV is negligible again. $PV_{\text{gas}} = n R T = 0.75 \text{ mol} \cdot 8.31451 \text{ J/mol K} \cdot 260 \text{ K} = 1.621 \text{ kJ}$. Thus the $\Delta U = \Delta H - PV_{\text{gas}} = 23.978 \text{ kJ} - 1.621 \text{ kJ} = 22.357 \text{ kJ}$. To find the work we need to assume that the pressure is constant and $w = -p_{\text{ex}} \Delta V$. Assuming that $\Delta V = V_{\text{gas}} - V_{\text{liquid}} = V_{\text{gas}}$, $w = -p_{\text{ex}} V_{\text{gas}} = -n R T = -1.621 \text{ kJ}$.

5. A sample of a liquid of mass 25 g is cooled from 290 K to 275 K at constant pressure by extraction of 2.3 kJ of energy as heat. Calculate q and ΔH and estimate the heat capacity of the sample.

At constant pressure (note heat was extracted, thus negative sign) $q = \Delta H = -2.3 \text{ kJ} = m C_p \Delta T = 25 \text{ g} \cdot C_p \cdot -15 \text{ K}$. Solving for $C_p = 6.13 \text{ J/g K}$.

Choose two of the following three problems for 45 points each:

6. A 0.2560 g sample of $C_7H_{15}COOH$ was burned in a constant volume oxygen bomb calorimeter. A total of 1132 J of energy was released to the water bath and bomb (observed by a temperature change). Calculate ΔH for the reaction. Assuming that all of the carbon and hydrogen were converted into gaseous CO_2 and liquid H_2O respectively, determine $\Delta_f H$ for $C_7H_{15}COOH$. ($\Delta_f H_{CO_2} = -393 \text{ kJ/mol}$, $\Delta_f H_{H_2O} = -285 \text{ kJ/mol}$)

Reaction may be written as: $C_7H_{15}COOH + 11 O_2 \rightarrow 8 CO_2 + 8 H_2O$.

Since constant volume $\Delta U = q = -1132 \text{ J}$. $\Delta U_m = -1132 \text{ J} / (0.2560 \text{ g} / 144.211 \text{ g/mol}) = -637.7 \text{ kJ/mol}$. To convert to ΔH we need to consider the $R T \Delta n = 8.31451 \text{ J/mol K} \cdot 298 \text{ K} \cdot -3 = -7.4 \text{ kJ/mol}$ (note that the -3 is a result of loss of 3 gas molecules per mole of reaction). The $\Delta_{rxn} H = -637.7 \text{ kJ/mol} - 7.4 \text{ kJ/mol} = -645.1 \text{ kJ/mol}$. To get the $\Delta_f H = 8 \Delta_f H_{H_2O} + 8 \Delta_f H_{CO_2} - 11 \Delta_f H_{O_2} - \Delta_{rxn} H = -4786 \text{ kJ/mol}$.

7. Assume that the heat capacity of a gas may be written as $C_p = A + B T + C T^2$ where $A = 28.0 \text{ J mol}^{-1} \text{ K}^{-1}$, $B = 0.021 \text{ J mol}^{-1} \text{ K}^{-2}$, $C = 0.00051 \text{ J mol}^{-1} \text{ K}^{-3}$. Calculate the ΔH when this gas is heated from 200 K to 400 K under constant pressure conditions.

$dH = C_p dT$, which must be integrated over the temperature range. Using the formula and integrating $\Delta H = (28.0 \text{ J mol}^{-1} \text{ K}^{-1}) (400 - 200 \text{ K}) + (0.021 \text{ J mol}^{-1} \text{ K}^{-2}) (400 - 200 \text{ K})^2 / 2 + (0.00051 \text{ J mol}^{-1} \text{ K}^{-3}) (400 - 200 \text{ K})^3 / 3 = 7380 \text{ J/mol}$.

8. The thermodynamic equation of state $(dU/dV)_T = T (dp/dT)_V - p$ was quoted in the text of chapter 3. Derive its partner: $(dH/dp)_T = -T (dV/dT)_p + V$ using $(dU/dV)_T$ and other derivative relationships.

$$\begin{aligned} (dH/dp)_T &= (dU/dp)_T + (d(pV)/dp)_T = (dU/dp)_T + p (dV/dp)_T + V(dp/dp)_T \\ &= (dU/dV)_T (dV/dp)_T + p (dV/dp)_T + V \\ &= (T (dp/dT)_V - p) (dV/dp)_T + p (dV/dp)_T + V \\ &= T (dp/dT)_V (dV/dp)_T - p (dV/dp)_T + p (dV/dp)_T + V \\ &= T (dp/dT)_V (dV/dp)_T + V = T (dp/dT)_V (-dV/dT)_p (dT/dp)_V + V \\ &= -T (dV/dT)_p (dp/dT)_V (dT/dp)_V + V = -T (dV/dT)_p + V \end{aligned}$$