

Chem 155

Problem Set #1

2002

**Handed out in class on September 6
Due in class on September 18**

The following problems are taken from Volume I, pp. 117-119

(4) 4.10

(10) 4.13

(4) 4.14

(4) 4.16

(10) 4.17

(10) 4.22

(8) 4.25

(10) 4.32

(25) 4.35

(15) 4.37

4.10 $\Delta U = 0$ for an ideal gas undergoing an isothermal process. Using this information, q can be calculated from w , the work done on the system.

$$w = (\text{force}) (\text{distance}) = (85 \text{ N}) (0.24 \text{ m}) = 20 \text{ J}$$

Because $\Delta U = 0 = q + w$, $q = -w = -20 \text{ J}$.

4.13 A 1.00-mole sample of ammonia at 14.0 atm and 25°C in a cylinder fitted with a movable piston expands against a constant external pressure of 1.00 atm. At equilibrium, the pressure and volume of the gas are 1.00 atm and 23.5 L, respectively. (a) Calculate the final temperature of the sample. (b) Calculate the values of q , w , and ΔU for the process.

(a) Assume ammonia is an ideal gas. The final temperature is

$$T_2 = \frac{P_2 V_2}{nR} = \frac{(1.00 \text{ atm}) (23.5 \text{ L})}{(1.00 \text{ mol}) (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})} = 286 \text{ K}$$

(b) The problem provides enough information to calculate w and ΔU directly. Consequently, q can be determined using the first law of thermodynamics.

w is related to the change in volume of the system. The final volume is given, but the initial volume needs to be calculated from the ideal gas law:

$$V_1 = \frac{nRT_1}{P_1} = \frac{(1.00 \text{ mol}) (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) (298 \text{ K})}{14.0 \text{ atm}} = 1.75 \text{ L}$$

The work done is

$$w = -P_{\text{ex}} \Delta V = -(1.00 \text{ atm}) (23.5 \text{ L} - 1.75 \text{ L}) \left(\frac{101.3 \text{ J}}{1 \text{ L atm}} \right) = -2.20 \times 10^3 \text{ J}$$

ΔU is related to C_V , which can be calculated from $\bar{C}_p = 35.66 \text{ J K}^{-1} \text{ mol}^{-1}$ listed in Appendix B. It is assumed that C_V and C_p are independent of temperature.

$$C_V = C_p - nR = (1.00 \text{ mol}) (35.66 \text{ J K}^{-1} \text{ mol}^{-1}) - (1.00 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = 27.35 \text{ J K}^{-1}$$

The change in internal energy is

$$\Delta U = C_V \Delta T = (27.35 \text{ J K}^{-1}) (286 \text{ K} - 298 \text{ K}) = -3.3 \times 10^2 \text{ J}$$

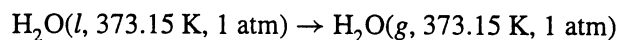
Using the first law of thermodynamics,

$$q = \Delta U - w = -3.3 \times 10^2 \text{ J} - (-2.20 \times 10^3 \text{ J}) = 1.87 \times 10^3 \text{ J}$$

4.14 An ideal gas is compressed isothermally from 2.0 atm and 2.0 L to 4.0 atm and 1.0 L. Calculate the values of ΔU and ΔH if the process is carried out (a) reversibly and (b) irreversibly.

ΔU and ΔH of an ideal gas depend only on T . Therefore, for any isothermal process [either process (a) or (b)], $\Delta U = 0$ and $\Delta H = 0$.

- 4.17 At 373.15 K and 1 atm, the molar volume of liquid water and steam are $1.88 \times 10^{-5} \text{ m}^3$ and $3.06 \times 10^{-2} \text{ m}^3$, respectively. Given that the heat of vaporization of water is $40.79 \text{ kJ mol}^{-1}$, calculate the values of ΔH and ΔU for 1 mole in the following process:



ΔH for the above process is the heat of vaporization, that is, $\Delta H = 40.79 \text{ kJ}$ for 1 mole of water.

It is necessary to calculate w and q before determining ΔU . Since the process occurs at constant pressure, $q = \Delta H = 40.79 \text{ kJ}$ when 1 mol liquid H_2O vaporizes. In the same process,

$$\begin{aligned} w &= -P_{\text{ex}} \Delta V \\ &= -(1.00 \text{ atm}) (3.06 \times 10^{-2} \text{ m}^3 - 1.88 \times 10^{-5} \text{ m}^3) \left(\frac{1000 \text{ L}}{1 \text{ m}^3} \right) \left(\frac{101.3 \text{ J}}{1 \text{ L atm}} \right) \\ &= -3.098 \times 10^3 \text{ J} \end{aligned}$$

Note that we could have safely ignored the volume of liquid H_2O , since it is negligible compared with that of gaseous H_2O above.

Using the first law,

$$\Delta U = q + w = 40.79 \text{ kJ} - 3.098 \text{ kJ} = 37.69 \text{ kJ}$$

- 4.22 A 10.0-g sheet of gold with a temperature of 18.0°C is laid flat on a sheet of iron that weighs 20.0 g and has a temperature of 55.6°C . Given that the specific heats of Au and Fe are $0.129 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ and $0.444 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$, respectively, what is the final temperature of the combined metals? Assume that no heat is lost to the surroundings. (*Hint:* The heat gained by the gold must be equal to the heat lost by the iron.)

The final temperature of the sheet of gold is the same as that of the sheet of iron when thermal equilibrium is reached, and is denoted by T_f . Furthermore, the amount of heat gained by gold is the same as that lost by iron, that is,

$$q_{\text{Au}} = -q_{\text{Fe}}$$

$$\begin{aligned} 4.16 \quad w < 0 \quad q < 0 \\ \Delta U < 0 \quad \Delta H < 0 \end{aligned}$$

The “-” sign is used to indicate that q_{Au} and q_{Fe} are of opposite sign.

The above relation gives

$$\begin{aligned}
 m_{\text{Au}} s_{\text{Au}} \Delta T_{\text{Au}} &= -m_{\text{Fe}} s_{\text{Fe}} \Delta T_{\text{Fe}} \\
 (10.0 \text{ g}) (0.129 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1}) (T_f - 18.0^\circ\text{C}) &= -(20.0 \text{ g}) (0.444 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1}) (T_f - 55.6^\circ\text{C}) \\
 (1.29 \text{ J } ^\circ\text{C}^{-1}) (T_f - 18.0^\circ\text{C}) &= -(8.88 \text{ J } ^\circ\text{C}^{-1}) (T_f - 55.6^\circ\text{C}) \\
 T_f - 18.0^\circ\text{C} &= -\frac{8.88 \text{ J } ^\circ\text{C}^{-1}}{1.29 \text{ J } ^\circ\text{C}^{-1}} (T_f - 55.6^\circ\text{C}) \\
 &= -6.884 (T_f - 55.6^\circ\text{C}) \\
 &= -6.884 T_f + 382.8^\circ\text{C} \\
 7.884 T_f &= 400.8^\circ\text{C} \\
 T_f &= 50.8^\circ\text{C}
 \end{aligned}$$

4.25 The constant-pressure molar heat capacity of nitrogen is given by the expression

$$\bar{C}_p = (27.0 + 5.90 \times 10^{-3} T - 0.34 \times 10^{-6} T^2) \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate the value of ΔH for heating 1 mole of nitrogen from 25.0°C to 125°C .

Since \bar{C}_p is temperature dependent, it has to be integrated over T to yield ΔH :

$$\begin{aligned}
 \Delta H &= \int_{298 \text{ K}}^{398 \text{ K}} n \bar{C}_p dT \\
 &= \int_{298 \text{ K}}^{398 \text{ K}} (1 \text{ mol}) [(27.0 + 5.90 \times 10^{-3} T - 0.34 \times 10^{-6} T^2) \text{ J K}^{-1} \text{ mol}^{-1}] dT \\
 &= \left[27.0T + 5.90 \times 10^{-3} \frac{T^2}{2} - 0.34 \times 10^{-6} \frac{T^3}{3} \right]_{298 \text{ K}}^{398 \text{ K}} \text{ J} \\
 &= \left[27.0(398) + 5.90 \times 10^{-3} \frac{398^2}{2} - 0.34 \times 10^{-6} \frac{398^3}{3} \right] \text{ J} \\
 &\quad - \left[27.0(298) + 5.90 \times 10^{-3} \frac{298^2}{2} - 0.34 \times 10^{-6} \frac{298^3}{3} \right] \text{ J} \\
 &= 2.90 \times 10^3 \text{ J}
 \end{aligned}$$

- 4.32 The equation of state for a certain gas is given by $P[(V/n) - b] = RT$. Obtain an expression for the maximum work done by the gas in a reversible isothermal expansion from V_1 to V_2 .

Write P in terms of n , V , and T :

$$P = \frac{RT}{\frac{V}{n} - b} = \frac{nRT}{V - nb}$$

The maximum work done by the gas undergoing an isothermal expansion is

$$\begin{aligned} w &= - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \frac{nRT}{V - nb} dV \\ &= -nRT \ln(V - nb) \Big|_{V_1}^{V_2} \\ &= -nRT \ln \frac{V_2 - nb}{V_1 - nb} \end{aligned}$$

- 4.35 One mole of an ideal monatomic gas initially at 300 K and a pressure of 15.0 atm expands to a final pressure of 1.00 atm. The expansion can occur via any of four different paths: (a) isothermal and reversible, (b) isothermal and irreversible, (c) adiabatic and reversible, and (d) adiabatic and irreversible. In irreversible processes, the expansion occurs against an external pressure of 1.00 atm. For each case calculate the values of q , w , ΔU , and ΔH .

(a) When an ideal gas undergoes an isothermal process, $\Delta U = 0$ and $\Delta H = 0$.

$$w = -nRT \ln \frac{P_1}{P_2} = - (1 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \ln \frac{15.0 \text{ atm}}{1.00 \text{ atm}} = -6.75 \times 10^3 \text{ J}$$

$$q = \Delta U - w = -w = 6.75 \times 10^3 \text{ J}$$

(b) When an ideal gas undergoes an isothermal process, $\Delta U = 0$ and $\Delta H = 0$.

$$w = -P_{\text{ex}} (V_2 - V_1)$$

V_1 and V_2 can be determined using the ideal gas law:

$$V_1 = \frac{nRT}{P_1} = \frac{(1 \text{ mol}) (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) (300 \text{ K})}{15.0 \text{ atm}} = 1.641 \text{ L}$$

$$V_2 = \frac{nRT}{P_2} = \frac{(1 \text{ mol}) (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) (300 \text{ K})}{1.00 \text{ atm}} = 24.62 \text{ L}$$

Therefore,

$$w = - (1.00 \text{ atm}) (24.62 \text{ L} - 1.641 \text{ L}) \left(\frac{101.3 \text{ J}}{1 \text{ L atm}} \right) = -2.33 \times 10^3 \text{ J}$$

and

$$q = \Delta U - w = -w = 2.33 \times 10^3 \text{ J}$$

(c) $q = 0$ for an adiabatic process.

To determine ΔU and ΔH , T_2 needs to be calculated. Using the same procedure as Problem 4.34(a),

$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} = (300 \text{ K}) \left(\frac{1.00 \text{ atm}}{15.0 \text{ atm}} \right)^{(\frac{5}{3}-1)/\frac{5}{3}} = 101.6 \text{ K}$$

Now the rest of the quantities can be calculated:

$$\Delta U = \overset{\text{or } n \bar{C}_V \Delta T}{C_V \Delta T} = \frac{3}{2} (1 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (101.6 \text{ K} - 300 \text{ K}) = -2.47 \times 10^3 \text{ J}$$

$$w = \Delta U - q = \Delta U = -2.47 \times 10^3 \text{ J}$$

$$\Delta H = \overset{\uparrow}{C_P \Delta T} = \frac{5}{2} (1 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (101.6 \text{ K} - 300 \text{ K}) = -4.12 \times 10^3 \text{ J}$$

$$\text{or } n \bar{C}_P \Delta T$$

(d) $q = 0$ for an adiabatic process.

See attached note for solving T_2

To determine ΔU and ΔH , T_2 needs to be calculated. Using the same procedure as Problem 4.34(b),

$$\begin{aligned} T_2 &= \frac{2}{5} \left(\frac{P_2}{P_1} + \frac{3}{2} \right) T_1 \\ &= \frac{2}{5} \left(\frac{1.00 \text{ atm}}{15.0 \text{ atm}} + \frac{3}{2} \right) (300 \text{ K}) = 188 \text{ K} \end{aligned}$$

Now the rest of the quantities can be calculated:

$$\Delta U = C_V \Delta T = \frac{3}{2} (1 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (188 \text{ K} - 300 \text{ K}) = -1.40 \times 10^3 \text{ J}$$

$$w = \Delta U - q = \Delta U = -1.40 \times 10^3 \text{ J}$$

$$\Delta H = C_P \Delta T = \frac{5}{2} (1 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (188 \text{ K} - 300 \text{ K}) = -2.33 \times 10^3 \text{ J}$$

Hint for solving Prob 4.35 (d)

To calculate the work done in an adiabatic, irreversible gas expansion, we need to know the final temperature. The conditions are:

Initial

$$T_1 = 300 \text{ K}$$

$$P_1 = 15.0 \text{ atm}$$

$$n = 1 \text{ mol}$$

$$V_1 = \frac{nRT_1}{P_1}$$

Final

$$T_2 = ?$$

$$P_2 = 1.00 \text{ atm}$$

Irreversible process

$$\begin{aligned} w = \Delta U &= C_V (T_2 - T_1) = -P_2 (V_2 - V_1) \\ &= n \bar{C}_V (T_2 - T_1) = -P_2 (V_2 - V_1) \end{aligned}$$

For a monatomic gas, $\bar{C}_V = \frac{3}{2}R$, so

$$\begin{aligned} \frac{3}{2} nR (T_2 - T_1) &= -P_2 (V_2 - V_1) \\ &= -P_2 \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right) \end{aligned}$$

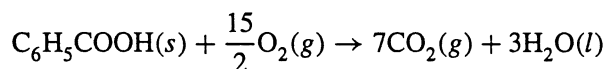
$$\frac{3}{2} (T_2 - T_1) = -T_2 + \frac{P_2}{P_1} T_1$$

Now you can solve for T_2 and hence ΔU

$$T_2 = \frac{2}{5} \left(\frac{P_2}{P_1} + \frac{3}{2} \right) T_1$$

4.37 The enthalpy of combustion of benzoic acid (C_6H_5COOH) is commonly used as the standard for calibrating constant-volume bomb calorimeters; its value has been accurately determined to be $-3226.7 \text{ kJ mol}^{-1}$. (a) When 0.9862 g of benzoic acid was oxidized, the temperature rose from 21.84°C to 25.67°C . What is the heat capacity of the calorimeter? (b) In a separate experiment, 0.4654 g of α -D-glucose ($C_6H_{12}O_6$) was oxidized in the same calorimeter and the temperature rose from 21.22°C to 22.28°C . Calculate the enthalpy of combustion of glucose, the value of $\Delta_r U$ for the combustion, and the molar enthalpy of formation of glucose.

(a) In a constant-volume calorimeter, the energy of combustion of benzoic acid, $\Delta_r U^\circ$, is the same as heat given off by the reaction, q , which is absorbed by the calorimeter. Therefore, the given value for the enthalpy of combustion must be converted to the energy of combustion. The combustion reaction for benzoic acid is



and has $\Delta n = -0.5 \text{ mol}$. From this, $\Delta_r U^\circ$ is found.

$$\begin{aligned}\Delta_r U^\circ &= \Delta_r H^\circ - RT \Delta n \\ &= -3226.7 \text{ kJ mol}^{-1} - (8.314 \text{ JK}^{-1} \text{ mol}^{-1})(298.15 \text{ K})(-0.5 \text{ mol}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \\ &= -3225.46 \text{ kJ mol}^{-1}\end{aligned}$$

Therefore,

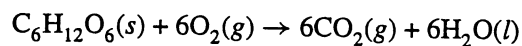
$$\begin{aligned}q_{\text{calorimeter}} &= -q_{\text{benzoic acid}} \\ C_{\text{calorimeter}} (25.67^\circ\text{C} - 21.84^\circ\text{C}) &= -\left(\frac{0.9862 \text{ g}}{122.1 \text{ g mol}^{-1}}\right) (-3225.46 \text{ kJ mol}^{-1}) \\ C_{\text{calorimeter}} &= \frac{26.052 \text{ kJ}}{3.83^\circ\text{C}} = 6.802 \text{ kJ }^\circ\text{C}^{-1}\end{aligned}$$

(b) In this experiment, the calorimeter absorbs heat transferred from the combustion of glucose.

$$\begin{aligned}q_{\text{calorimeter}} &= -q_{\text{glucose}} \\ 6.802 \text{ kJ }^\circ\text{C}^{-1} (22.28^\circ\text{C} - 21.22^\circ\text{C}) &= -\left(\frac{0.4654 \text{ g}}{180.2 \text{ g mol}^{-1}}\right) (\Delta_r U^\circ) \\ \Delta_r U^\circ &= -2.79 \times 10^3 \text{ kJ mol}^{-1}\end{aligned}$$

The First Law of Thermodynamics

To calculate the enthalpy of combustion, the change in number of moles of gases in the reaction has to be determined. The reaction is



so $\Delta n = 0$. Therefore,

$$\Delta_r H^\circ = \Delta_r U^\circ + RT \Delta n = \Delta_r U^\circ = -2.79 \times 10^3 \text{ kJ mol}^{-1}$$

The molar enthalpy of formation is related to $\Delta_r H^\circ$ of the combustion reaction.

$$\begin{aligned}\Delta_r H^\circ &= 6\Delta_f \bar{H}^\circ [\text{CO}_2(g)] + 6\Delta_f \bar{H}^\circ [\text{H}_2\text{O}(l)] - \Delta_f \bar{H}^\circ [\text{C}_6\text{H}_{12}\text{O}_6(s)] \\ &\quad - 6\Delta_f \bar{H}^\circ [\text{O}_2(g)] \\ \Delta_f \bar{H}^\circ [\text{C}_6\text{H}_{12}\text{O}_6(s)] &= 6\Delta_f \bar{H}^\circ [\text{CO}_2(g)] + 6\Delta_f \bar{H}^\circ [\text{H}_2\text{O}(l)] - 6\Delta_f \bar{H}^\circ [\text{O}_2(g)] - \Delta_r H^\circ \\ &= 6(-393.5 \text{ kJ mol}^{-1}) + 6(-285.8 \text{ kJ mol}^{-1}) - 6(0 \text{ kJ mol}^{-1}) \\ &\quad - (-2.79 \times 10^3 \text{ kJ mol}^{-1}) \\ &= -1.29 \times 10^3 \text{ kJ mol}^{-1}\end{aligned}$$