Chemistry 431
Problem Set 5
Fall 2023
Solutions

1. Use Tables 4.1 and 4.2 to calculate the enthalpy of the reaction

   $C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)}$

   at 25.°C.
   Answer:

$$\Delta_{r,m}H^{\ominus} = \Delta_{f,m}H^{\ominus}(C_2H_6) - 2\Delta_{f,m}H^{\ominus}(H_2) - \Delta_{f,m}H^{\ominus}(C_2H_2)$$

$$= [-84. - 2(0) - 227.4] \text{ kJ mol}^{-1} = -311.4 \text{ kJ mol}^{-1}$$

2. Use Tables 4.1 and 4.2 to determine the enthalpy of the reaction of problem 1 at 35.°C. You may assume the heat capacities given in the table are independent of temperature.
   Answer:

$$\Delta_{r,m}H^{\ominus}(T_2) = \Delta_{r,m}H^{\ominus}(T_1) + \Delta C_p \Delta T$$

$$= -311400 \text{ J mol}^{-1} + [C_p(C_2H_6) - 2C_p(H_2) - C_p(C_2H_2)]10\text{K}$$

$$= -311400 \text{ J mol}^{-1} + [52.5 - 2(28.8) - 44.] \text{ J mol}^{-1}\text{K}^{-1}(10 \text{ K}) = -311.891 \text{ kJ mol}^{-1}$$

3. The enthalpy of combustion of liquid d-citrene ($C_{10}H_{16}$) is ΔH = -420.79 kJ mol^{-1} at 298. K. Use Tables 4.1 and 4.2 to determine the enthalpy of formation of liquid d-citrene.
   Answer:

$$C_{10}H_{16(l)} + 14O_{2(g)} \longrightarrow 10CO_{2(g)} + 8H_2O_{(l)}$$

$$\Delta_{r,m}H^{\ominus} = 8\Delta_{f,m}H^{\ominus}(H_2O_{(l)}) + 10\Delta_{f,m}H^{\ominus}(CO_{2(g)}) - \Delta_{f,m}H^{\ominus}(C_{10}H_{16(l)}) - 14\Delta_{f,m}H^{\ominus}(O_{2(g)})$$

$$-420.79 \text{ kJ mol}^{-1} = 8(-285.8 \text{ kJ mol}^{-1}) + 10(-393.5 \text{ kJ mol}^{-1}) - \Delta_{f,m}H^{\ominus}(C_{10}H_{16(l)})$$

$$\Delta_{f,m}H^{\ominus}(C_{10}H_{16(l)}) = -5801 \text{ kJ mol}^{-1}$$

4. Use the data from problem 3 to determine the heat liberated if 10.0 g of liquid d-citrene are burned in a bomb calorimeter thermostated to 298. K.
   Answer:

$$\Delta_{r,m}U = \Delta_{r,m}H - RT\Delta n_{gas}$$

$$= -420790 \text{ J mol}^{-1} - (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})(-4)$$

$$= -410990 \text{ J mol}^{-1}$$

$$q = (10 \text{ g}) \left(\frac{\text{mol}}{136 \text{ g}} \right) (-410990 \text{ J mol}^{-1}) = -30.2 \text{ kJ}$$

5. When exactly 0.015 moles of H_2 gas and 0.005 moles of N_2 gas at 25.°C react adiabatically and completely to form pure NH_3 gas in a container of fixed volume, the final temperature of the product is found to be 1860.K. Assuming only the temperature of the product gas changes and the temperature of the insulating chamber does not change, calculate the molar enthalpy of formation of $NH_{3(g)}$ at 298K. You should assume the molar constant volume heat capacity of $NH_{3(g)}$ to be a constant and equal to 27.8 J $\text{mol}^{-1}\text{K}^{-1}$, and that all gases are ideal.
   Answer:
   $$\frac{3}{2}H_{2(g)} + \frac{1}{2}N_{2(g)} \longrightarrow NH_{3(g)}$$
   Then 0.01 moles of ammonia gas are formed.
   $$\Delta U = -(.01 \text{ mol})(27.8 \text{ J mol}^{-1}\text{K}^{-1})(1860 \text{ K} - 298 \text{ K}) = -434.2 \text{ J}$$
   $$\Delta_m U = \frac{-434.2 \text{ J}}{0.01 \text{ mol}} = -43424. \text{ J mol}^{-1}$$
   $$\Delta_m H = \Delta U_m + RT\Delta n_{gas}$$
   $$= -43424. \text{ J mol}^{-1} + (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})(-1) = -45900 \text{ J mol}^{-1}$$

6. The standard enthalpy of formation of $PH_{3(g)}$ is 5.400 kJ per mole of $PH_{3(g)}$ at 298K and 3.158 kJ per mole of $PH_{3(g)}$ at 373K. Given the constant pressure heat capacities of solid white phosphorous (the most stable form of elemental phosphorous at 1 bar pressure the both conditions of temperature) and $PH_{3(g)}$ are respectively 23.8 J $\text{mol}^{-1}\text{K}^{-1}$ and 37.1 J $\text{mol}^{-1}\text{K}^{-1}$, calculate the constant pressure heat capacity of hydrogen gas. Assume all heat capacities are temperature independent. Compare the determined constant pressure heat capcity of H_2 with that expected for an ideal diatomic gas.
   Answer:
   $$P_{(s,w)} + \frac{3}{2}H_{2(g)} \longrightarrow PH_{3(g)}$$
   $$\Delta_{f,m}H^{\ominus}(373\,\text{K}) = \Delta_{f,m}H^{\ominus}(298\,\text{K}) + \left[C_{P,m}(PH_{3(g)}) - C_{P,m}(P_{s,w}) - \frac{3}{2}C_{P,m}(H_{2(g)})\right]\Delta T$$
   $$3158\text{ J mol}^{-1} = 5400\text{ J mol}^{-1} + (75.\text{ K})\left[37.1\text{ J mol}^{-1}\text{K}^{-1} - 23.8\text{ J mol}^{-1}\text{K}^{-1} - \frac{3}{2}C_{P,m}(H_{2(g)})\right]$$
   $$C_{P.m}(H_{2(g)}) = 28.8 \text{ J mol}^{-1}\text{K}^{-1}$$
   $$\frac{7}{2}R = \frac{7}{2}(8.3144 \text{ J mol}^{-1}\text{K}^{-1}) = 29.1 \text{ J mol}^{-1}\text{K}^{-1}$$

7. Calculate the heat liberated to the surroundings when 10.0 grams of liquid ethanol (C_2H_5OH) are burned in pure oxygen gas to produce CO_2 gas and H_2O liquid in a bomb calorimeter of fixed volume with the thermostat set to 100.°C. The required data are found in Tables 4.1 and 4.2 of the textbook.
   Answer:
$$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$$
$$\Delta_{r,m}H^{\ominus}(298\text{K}) = [2(-393.5) + 3(-285.8) - (-277.6)] \text{ kJ mol}^{-1} = -1366.8 \text{ kJ mol}^{-1}$$
$$\Delta_{r,m}H^{\ominus}(373 \text{ K}) = \Delta_{r,m}H^{\ominus}(298 \text{ K}) + \Delta C_P \Delta T$$
$$= -1366800 \text{ J mol}^{-1} + [3(75.3)+2(37.1)-3(29.4)-112.2] \text{ J mol}^{-1}\text{K}^{-1}(75 \text{ K}) = -1359322 \text{ J mol}^{-1}$$
$$\Delta_{r,m}U(373 \text{ K}) = \Delta_{r,m}H^{\ominus}(373 \text{ K}) - RT\Delta n_{gas} = -1359322 \text{ J mol}^{-1} - (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(373 \text{ K})(-1$$
$$= -1356221 \text{ J mol}^{-1}$$
$$n = \frac{10 \text{ g}}{46 \text{ g mol}^{-1}} = 0.217 \text{ mol}$$
$$q_{sys} = \Delta U = (0.217 \text{ mol})(-1356221 \text{ J mol}^{-1}) = -294830 \text{ J}$$
$$q_{surr} = -q_{sys} = 294830 \text{ J}$$

8. A large metal bomb calorimeter of constant volume is known to have a heat capacity of 28749. J K^{-1}. When exactly 5.0 grams of solid benzoic acid (C_6H_5COOH) are placed in the bomb with excess oxygen gas at 25.0°C, and combusted adiabatically to produce gas phase carbon dioxide and liquid phase water, the temperature rise of the calorimeter is found to be 4.60K. Assuming the reactants and products contribute negligibly to the overall heat capacity of the system, calculate the molar enthalpy change of combustion reaction for the benzoic acid at 25.0°C.
   Answer:
$$C_6H_5COOH_{(s)} + \frac{15}{2}O_{2(g)} \longrightarrow 7CO_{2(g)} + 3H_2O_{(\ell)}$$
$$q = \Delta_r U = -C\Delta T = -(28749 \text{ J K}^{-1})(4.6 \text{ K}) = -132245.4 \text{ J}$$
$$n = \frac{5.0 \text{ g}}{122. \text{ g mol}^{-1}} = 0.0410 \text{ mol}$$
$$\Delta_{r,m}U = \frac{-132245.4 \text{ J}}{0.0410 \text{ mol}} = -3226787.8 \text{ J mol}^{-1}$$
$$\Delta_{r,m}H = \Delta U_{r,m} + RT\Delta n_{gas}$$
$$= -3226787.8 \text{ J mol}^{-1} + (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})\left(-\frac{1}{2}\right) = -3228027 \text{ J mol}^{-1}$$
$$= -3228.0 \text{ kJ mol}^{-1}$$

9. When 1.00 grams of gas-phase dimethyl ether [$(CH_3)_2O$] at 298. K are burned isothermally in excess pure oxygen to produce gas-phase water and gas-phase carbon dioxide under standard conditions of pressure, the heat liberated to the surroundings is measured to be 2882. Joules. Calculate the heat liberated to the surroundings if the same mixture of dimethyl ether and excess oxygen at 373. K are burned isothermally in a container of fixed volume. You can use the following table of thermodynamic data and assume the constant pressure heat capacities are temperature independent.

Substance	C_P (J mol^{-1}K^{-1})
$(CH_3)_2O_{(g)}$	64.4
$H_2O_{(g)}$	33.6
$CO_{2(g)}$	37.1
$O_{2(g)}$	29.4

Answer:

$$(CH_3)_2O_{(g)} + 3O_{2(g)} \longrightarrow 3H_2O_{(g)} + 2CO_{2(g)}$$

$$n = \frac{1.00 \text{ g}}{46.0 \text{ g mol}^{-1}} = 2.17 \times 10^{-2} \text{ mol}$$

$$\Delta_{r,m}H^{\ominus} = \frac{-2882. \text{ J}}{2.17 \times 10^{-2} \text{ mol}} = -132800 \text{ J mol}^{-1}$$

$$\Delta_{r,m}H^{\ominus}(373) = \Delta_{r,m}H^{\ominus}(298) + \Delta C_P \Delta T = -132800 \text{ J mol}^{-1}$$

$$+[3(33.6) + 2(37.1) - 3(29.4) - 64.4] \text{ J mol}^{-1}\text{K}^{-1}(75. \text{ K}) = -131120 \text{ J mol}^{-1}$$

$$\Delta_{r,m}U = \Delta_{r,m}H^{\ominus} - RT\Delta n_{gas}$$

$$= -131120 \text{ J mol}^{-1} - (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(373. \text{ K})(1) = -134221 \text{ J mol}^{-1}$$

$$q_{surr} = -\Delta U = (134221 \text{ J mol}^{-1})(2.17 \times 10^{-2} \text{ mol}) = 2913 \text{ J}$$

10. When 10.00 grams of liquid formic acid (HCOOH) are burned in pure oxygen producing gas-phase water and carbon dioxide in a container of fixed volume at a constant temperature of 25.0°C, the reaction is exothermic with $q = -55440.$ Joules. Calculate the heat associated with burning the 10.0 grams of liquid formic acid to produce the same products if the temperature is fixed at 35.0°C, and the reaction is carried out at a constant pressure of 1.00 bar. The constant pressure heat capacities are 99.0 J mol^{-1}K^{-1} for liquid formic acid, 37.1 J mol^{-1}K^{-1} for gas-phase carbon dioxide, 33.6 J mol^{-1}K^{-1} for gas-phase water and 29.4 J mol^{-1}K^{-1} for gas-phase oxygen. You can assume all values of C_P are temperature independent.

Answer:

$$HCOOH_{(\ell)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} + H_2O_{(g)}$$

$$n = \frac{10.00 \text{ g}}{46.00 \text{ g mol}^{-1}} = 0.2174 \text{ mol}$$

$$\Delta_{r,m}U = \frac{-55440 \text{ J}}{0.2174 \text{ mol}} = -255014 \text{ J mol}^{-1}$$

$$\Delta_{r,m}H^{\ominus}(298 \text{ K}) = \Delta_{r,m}U + RT\Delta n_{gas}$$

$$= -255014 \text{ J mol}^{-1} + (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298. \text{ K})(3/2) = -251297 \text{ J mol}^{-1}$$

$$\Delta_{r,m}H^{\ominus}(308 \text{ K}) = \Delta_{r,m}H^{\ominus}(298 \text{ K}) + \Delta C_P \Delta T$$

$$= -251297 \text{ J mol}^{-1}$$

$$+(33.6 \text{ J mol}^{-1}\text{K}^{-1} + 37.1 \text{ J mol}^{-1}\text{K}^{-1} - 99.0 \text{ J mol}^{-1}\text{K}^{-1} - 0.5\times 29.4 \text{ J mol}^{-1}\text{K}^{-1})(10. \text{ K})$$

$$= -251108 \text{ J mol}^{-1}$$

$$q = n\Delta_{r,m}H^{\ominus} = (-251108 \text{ J mol}^{-1})(0.2174 \text{ mol}) = -54591 \text{ J}$$

11. At 298K the standard enthalpy of combustion of solid phenol (C_6H_5OH) in pure oxygen gas to produce gas phase CO_2 and liquid water is $\Delta_{combustion,m}H^{\ominus} = -3054.$ kJ mol^{-1}. Use the table of constant pressure heat capacities given below to calculate the heat for the system for the combustion of 2.00 grams of phenol when the reaction takes place in a container of fixed volume at 323K.

Substance	C_P (J mol^{-1}K^{-1})
$C_6H_5OH_{(s)}$	127.4
$O_{2(g)}$	29.4
$CO_{2(g)}$	37.1
$H_2O_{(\ell)}$	75.3

Answer:

$$C_6H_5OH_{(s)} + 7O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(\ell)}$$

$$n = \frac{2.00 \text{ g}}{94.1 \text{ g mol}^{-1}} = 2.125 \times 10^{-2} \text{ mol}$$

$$\Delta_{r,m}H^{\ominus}(323\text{K}) = \Delta_{r,m}H^{\ominus}(298\text{K}) + \Delta C_P \Delta T$$

$$= -3054\times 10^3 \text{ J mol}^{-1} + [3(75.3)+6(37.1)-127.4-7(29.4)] \text{ J mol}^{-1}\text{K}^{-1}(25 \text{ K}) = -3051000 \text{ J mol}^{-1}$$

$$\Delta_{r,m}U = \Delta_{r,m}H^{\ominus} - RT\Delta n_{gas} = -3051000 \text{ J mol}^{-1} - (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(323 \text{ K})(-1) = -3048432 \text{ J}$$

$$q = n\Delta_{r,m}U = -64.8 \text{ kJ}$$

12. When 10.0 g of liquid-phase cyclohexane (C_6H_{12}) are burned in pure oxygen gas to produce gas-phase carbon dioxide and liquid water in a bomb calorimeter of fixed volume at a constant temperature of 350K, 463 kJ of heat are liberated to the surroundings. Use the table of thermodynamic data valid at 298K given below to calculate the standard enthalpy of formation of liquid-phase cyclohexane at 298K assuming the heat capacities of all species are temperature independent.

Substance	$\Delta_{f,m}H^\ominus$ kJ mol^{-1}	C_P (J mol^{-1}K^{-1})
$C_6H_{12(\ell)}$		154.9
$O_{2(g)}$		29.4
$H_2O_{(\ell)}$	-285.8	75.3
$CO_{2(g)}$	-393.5	37.1

Answer:

$$C_6H_{12(\ell)} + 9O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(\ell)}$$

$$n = \frac{10.0\ \text{g}}{84.0\ \text{g mol}^{-1}} = 0.119\ \text{mol}$$

$$q_m = \Delta_{r,m}U(350) = \frac{-463.\ \text{kJ}}{0.119\ \text{mol}} = -3891\ \text{kJ mol}^{-1}$$

$$\Delta_{r,m}H^\ominus(350) = \Delta_{r,m}U(350) + RT\Delta n_g$$

$$= -3891 \times 10^3\ \text{J mol}^{-1} + (8.3144\ \text{J mol}^{-1}\text{K}^{-1})(350\ \text{K})(-3) = -3899\ \text{kJ mol}^{-1}$$

$$\Delta_{r,m}H^\ominus(298) = \Delta_{r,m}H^\ominus(350) + \Delta C_P \Delta T$$

$$= -3899 \times 10^3\ \text{J mol}^{-1} + [6(75.3\ \text{J mol}^{-1}\text{K}^{-1}) + 6(37.1\ \text{J mol}^{-1}\text{K}^{-1})$$

$$-9(29.4\ \text{J mol}^{-1}\text{K}^{-1}) - 154.9\ \text{J mol}^{-1}\text{K}^{-1}] = -3912\ \text{kJ mol}^{-1}$$

$$= 6\Delta_{f,m}H^\ominus(H_2O_{(\ell)}) + 6\Delta_{f,m}H^\ominus(CO_{2(g)}) - 9\Delta_{f,m}H^\ominus(O_{2(g)}) - \Delta_{f,m}H^\ominus(C_6H_{12(\ell)})$$

$$\Delta_{f,m}H^\ominus(C_6H_{12(\ell)}) = 3912\ \text{kJ mol}^{-1} + 6(-285.8\ \text{kJ mol}^{-1}) + 6(-393.5\ \text{kJ mol}^{-1}) - 9(0)$$

$$= -163.8\ \text{kJ mol}^{-1}$$

13. When 1.00 grams of liquid methanol (CH_3OH) are burned in a container of fixed volume at 50.0°C in pure oxygen gas to produce gas-phase carbon dioxide and liquid water, the exothermic reaction releases 22650 Joules of heat to the surroundings. Given the constant pressure heat capacities of $CO_{2(g)}$, $H_2O_{(\ell)}$, $CH_3OH_{(\ell)}$ and $O_{2(g)}$ are respectively 37.1 J mol^{-1}K^{-1}, 75.3 J mol^{-1}K^{-1}, 44.1 J mol^{-1}K^{-1}, and 29.4 J mol^{-1}K^{-1}, calculate the molar enthalpy change for the reaction at 25.0°C. You can assume the constant pressure heat capacities of all species are independent of temperature.
Answer:

$$CH_3OH_{(\ell)} + \frac{3}{2}O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(\ell)}$$

$$n = \frac{1.00\ \text{g}}{32.0\ \text{g mol}^{-1}} = 0.0312\ \text{mol}$$

At 50.0°C

$$q_m = \Delta_{r,m}U = \frac{-22650\ \text{J}}{0.0312\ \text{mol}} = -724800\ \text{J mol}^{-1}$$

$$\Delta_{r,m}H^\ominus = \Delta U_{r,m} + RT\Delta n_{gas} = -724800\ \text{J mol}^{-1} + (8.3144\ \text{J mol}^{-1}\text{K}^{-1})(323.\ \text{K})(-1/2)$$

$$= -726143\ \text{J mol}^{-1}$$

At 25.0°C

$$\Delta_{r,m}H^{\ominus}(T_2) = \Delta_{r,m}H(T_1)^{\ominus} + \Delta C_P \Delta T$$

$$\Delta_{r,m}H^{\ominus}(298.\text{ K}) = -726143\text{ J mol}^{-1} + [37.1\text{ J mol}^{-1}\text{K}^{-1} + 2(75.3)\text{ J mol}^{-1}\text{K}^{-1} - 44.1\text{ J mol}^{-1}\text{K}^{-1}$$
$$-(3/2)(29.4)\text{ J mol}^{-1}\text{K}^{-1}](-25.0\text{ K}) = -728630\text{ J mol}^{-1}$$

14. Use the table of thermodynamic data below valid at 298 K to calculate the heat of the system associated with the combustion of 50.053 grams liquid cyclopentane (C_5H_{10}) in pure oxygen to produce carbon dioxide gas and gas-phase water in a bomb of fixed volume in a heat bath with the thermostat set to 298 K.

Substance	$\Delta_{f,m}H^{\ominus}$ (kJ mol)$^{-1}$
$CO_{2(g)}$	-393.5
$O_{2(g)}$	0
$H_2O_{(g)}$	-241.8
$C_5H_{10(\ell)}$	-105.1

Answer:

$$C_5H_{10(\ell)} + \frac{15}{2}O_{2(g)} \longrightarrow 5CO_{2(g)} + 5H_2O_{(g)}$$

$$\Delta_{r,m}H^{\ominus} = 5\Delta_{f,m}H^{\ominus}(CO_{2(g)}) + 5\Delta_{f,m}H^{\ominus}(H_2O_{(g)}) - \frac{15}{2}(0) - \Delta_{f,m}H^{\ominus}(C_5H_{10(\ell)})$$

$$= 5(-393.5\text{ kJ mol}^{-1}) + 5(-241.8\text{ kJ mol}^{-1}) - (-105.1\text{ kJ mol}^{-1}) = -3071.4\text{ kJ mol}^{-1}$$

$$\Delta U_{r,m} = \Delta_{r,m}H^{\ominus} - RT\Delta n_{gas}$$

$$= -3071.4 \times 10^3\text{ J mol}^{-1} - (8.3144\text{ J mol}^{-1}\text{K}^{-1})(298\text{ K})(2.5) = -3077.6\text{ kJ mol}^{-1}$$

$$n = \frac{50.053\text{ g}}{70.134\text{ g mol}^{-1}} = 0.7137\text{ mol}$$

$$q = n\Delta_{r,m}U = (0.7137\text{ mol})(-3077.6\text{ kJ mol}^{-1}) = -2196.5\text{ kJ}$$