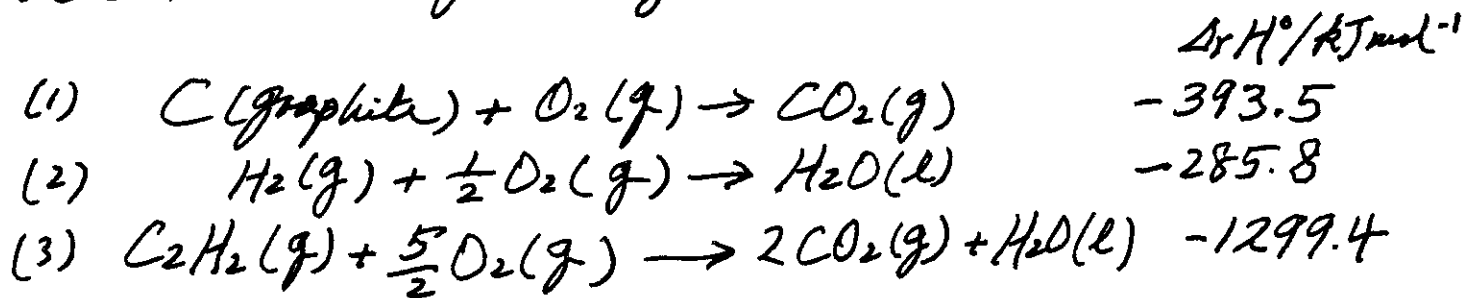


Problem Set #2

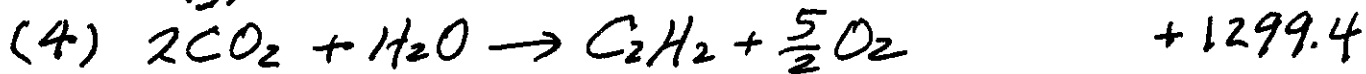
2002

The first problem.

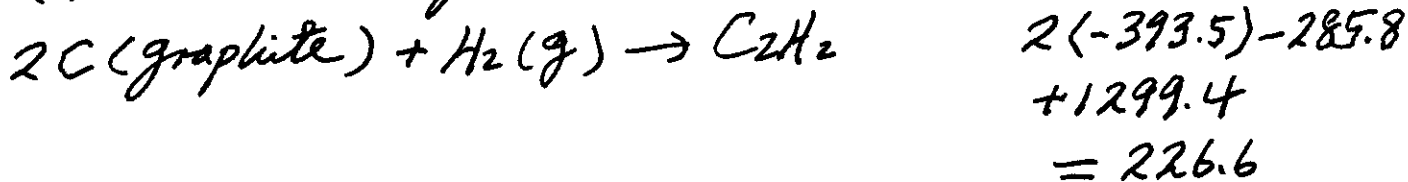
We know the following:



Reverse (3) ~~adds~~

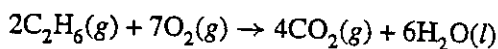


2 x (1) + (2) + (3) gives



Therefore, $\Delta_f \bar{H}^\circ(\text{C}_2\text{H}_2) = 226.6 \text{ kJ mol}^{-1}$

4.60 Use the bond enthalpy values in Table 4.4 to calculate the enthalpy of combustion for ethane,



Compare your result with that calculated from the enthalpy of formation values of the products and reactants listed in Appendix B.

Calculation of the enthalpy of combustion using bond enthalpies:

Type of bonds broken	Number of bonds broken	Bond enthalpy / $\text{kJ}\cdot\text{mol}^{-1}$	Enthalpy change / $\text{kJ}\cdot\text{mol}^{-1}$
C—H	12	414	4968
C—C	2	347	694
O=O	7	498.8	3491.6

Type of bonds formed	Number of bonds formed	Bond enthalpy / $\text{kJ}\cdot\text{mol}^{-1}$	Enthalpy change / $\text{kJ}\cdot\text{mol}^{-1}$
C=O	8	799	6392
O—H	12	460	5520

$$\Delta_r H^\circ = (4968 + 694 + 3491.6) \text{ kJ mol}^{-1} - (6392 + 5520) \text{ kJ mol}^{-1} = -2758 \text{ kJ mol}^{-1}$$

Calculation of the enthalpy of combustion using enthalpies of formation:

$$\begin{aligned} \Delta_r H^\circ &= 4\Delta_f \bar{H}^\circ [\text{CO}_2(g)] + 6\Delta_f \bar{H}^\circ [\text{H}_2\text{O}(l)] - 2\Delta_f \bar{H}^\circ [\text{C}_2\text{H}_6(g)] - 7\Delta_f \bar{H}^\circ [\text{O}_2(g)] \\ &= 4(-393.5 \text{ kJ mol}^{-1}) + 6(-285.8 \text{ kJ mol}^{-1}) - 2(-84.7 \text{ kJ mol}^{-1}) - 7(0 \text{ kJ mol}^{-1}) \\ &= -3119.4 \text{ kJ mol}^{-1} \end{aligned}$$

The value of $\Delta_r H^\circ$ so calculated is 13% greater than that calculated using bond enthalpies. The value determined using enthalpies of formation is the correct value, since it relies on the first law of thermodynamics. Bond enthalpies are averages determined for similar bonds in many molecules and provide estimates that are typically within 10% of the experimental value for any given, particular reaction.

- 5.5 The internal combustion engine of a 1200-kg car is designed to run on octane (C_8H_{18}), whose enthalpy of combustion is 5510 kJ mol^{-1} . If the car is moving up a slope, calculate the maximum height (in meters) to which the car can be driven on 1.0 gallon of the fuel. Assume that the engine cylinder temperature is 2200°C and the exit temperature is 760°C , and neglect all forms of friction. The mass of 1 gallon of fuel is 3.1 kg. [Hint: The work done in moving the car over a vertical distance is mgh , where m is the mass of the car in kg, g the acceleration due to gravity (9.81 m s^{-2}), and h the height in meters.]

To calculate the maximum height the car can be driven, the engine's capacity to do work must first be determined. This work is derived from the heat released by the combustion of octane, but remember the conversion from heat to work is limited by the efficiency of the engine.

$$q_{\text{octane}} = \text{Heat released by combustion of octane}$$

$$= (-5510 \text{ kJ mol}^{-1}) \left(\frac{1 \text{ mol}}{114.22 \times 10^{-3} \text{ kg}} \right) (3.1 \text{ kg}) = -1.50 \times 10^5 \text{ kJ}$$

$$q_{\text{engine}} = \text{heat absorbed by engine} = -q_{\text{octane}} = 1.50 \times 10^5 \text{ kJ}$$

$$\text{Net work done by engine} = |w_{\text{engine}}| = q_{\text{engine}} (\text{efficiency}) = q_{\text{engine}} \left(1 - \frac{T_1}{T_2} \right)$$

$$= (1.50 \times 10^5 \text{ kJ}) \left(1 - \frac{1033 \text{ K}}{2473 \text{ K}} \right) = 8.73 \times 10^4 \text{ kJ}$$

$$|w_{\text{engine}}| = 8.73 \times 10^7 \text{ J} = mgh = (1200 \text{ kg}) (9.81 \text{ m s}^{-2}) h$$

$$h = 7.4 \times 10^3 \text{ m}$$

- 5.8 One of the many statements of the second law of thermodynamics is: Heat cannot flow from a colder body to a warmer one without external aid. Assume two systems, 1 and 2, at T_1 and T_2 ($T_2 > T_1$). Show that if a quantity of heat q did flow spontaneously from 1 to 2, the process would result in a decrease in the entropy of the universe. (You may assume that the heat flows very slowly so that the process can be regarded as reversible. Assume also that the loss of heat by system 1 and the gain of heat by system 2 do not affect T_1 and T_2 .)

The universe is comprised of the two systems. Since heat flows from system 1 to 2, $q_1 = -q_{\text{rev}}$ and $q_2 = q_{\text{rev}}$.

$$\begin{aligned} \Delta S_{\text{univ}} &= \Delta S_1 + \Delta S_2 = \frac{q_1}{T_1} + \frac{q_2}{T_2} = \frac{-q_{\text{rev}}}{T_1} + \frac{q_{\text{rev}}}{T_2} \\ &= q_{\text{rev}} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) < 0 \quad \text{since } T_1 < T_2 \end{aligned}$$

5.15 Calculate the value of ΔS in heating 3.5 moles of a monatomic ideal gas from 50°C to 77°C at constant pressure.

At constant pressure,

$$\Delta S = n\bar{C}_p \ln \frac{T_2}{T_1} = \frac{5}{2}nR \ln \frac{T_2}{T_1} = \frac{5}{2}(3.5 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{323 \text{ K}}{323 \text{ K}} = 5.8 \text{ J K}^{-1}$$

5.19 The heat capacity of chlorine gas is given by

$$\bar{C}_p = (31.0 + 0.008T) \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate the entropy change when 2 moles of gas are heated from 300 K to 400 K at constant pressure.

$$\begin{aligned} \Delta S &= \int \frac{dq_{\text{rev}}}{T} = \int_{300 \text{ K}}^{400 \text{ K}} \frac{C_p dT}{T} \\ &= \int_{300 \text{ K}}^{400 \text{ K}} (2 \text{ mol}) \left(\frac{31.0 + 0.008T}{T} \text{ J K}^{-1} \text{ mol}^{-1} \right) dT \\ &= \left[2 \int_{300 \text{ K}}^{400 \text{ K}} \left(\frac{31.0}{T} + 0.008 \right) dT \right] \text{ J K}^{-1} \\ &= \left[(2) (31.0 \ln T + 0.008T) \right]_{300}^{400} \text{ J K}^{-1} \\ &= 2 \{ [31.0 \ln 400 + 0.008(400)] - [31.0 \ln 300 + 0.008(300)] \} \text{ J K}^{-1} \\ &= 19.4 \text{ J K}^{-1} \end{aligned}$$

5.27 A quantity of 0.35 mole of an ideal gas initially at 15.6°C is expanded from 1.2 L to 7.4 L. Calculate the values of w , q , ΔU , and ΔS if the process is carried out (a) isothermally and reversibly, and (b) isothermally and irreversibly against an external pressure of 1.0 atm.

(a) $\Delta U = 0$ for an isothermal process. Thus, $q = -w$.

$$\begin{aligned} w &= -nRT \ln \frac{V_2}{V_1} \\ &= -(0.35 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (288.8 \text{ K}) \ln \frac{7.4 \text{ L}}{1.2 \text{ L}} \\ &= -1.53 \times 10^3 \text{ J} \\ q &= 1.53 \times 10^3 \text{ J} \\ \Delta S &= \frac{q_{\text{rev}}}{T} = \frac{1.53 \times 10^3 \text{ J}}{288.8 \text{ K}} = 5.3 \text{ J K}^{-1} \end{aligned}$$

The final answers for q and w should be rounded to two significant figures, $q = 1.5 \times 10^3 \text{ J}$ and $w = -1.5 \times 10^3 \text{ J}$.

(b) $\Delta U = 0$ for an isothermal process. Thus, $q = -w$.

$$\begin{aligned} w &= -P_{\text{ex}} \Delta V = -(1.0 \text{ atm}) (7.4 \text{ L} - 1.2 \text{ L}) \left(\frac{101.3 \text{ J}}{1 \text{ L atm}} \right) = -6.28 \times 10^2 \text{ J} \\ q &= 6.28 \times 10^2 \text{ J} \\ \Delta S &= 5.3 \text{ J K}^{-1} \text{ [as calculated in Part (a).]} \end{aligned}$$

Recall that S is a state function, but ΔS has to be calculated using a reversible path. Again, the final answers for q and w should be rounded to two significant figures, $q = 6.3 \times 10^2 \text{ J}$ and $w = -6.3 \times 10^2 \text{ J}$.

5.40 Calculate the entropy change when neon at 25°C and 1.0 atm in a container of volume 0.780 L is allowed to expand to 1.25 L and is simultaneously heated to 85°C. Assume ideal behavior. (*Hint:* Because S is a state function, you can first calculate the value of ΔS for expansion and then calculate the value of ΔS for heating at constant final volume.)

The number of moles of Ne can be determined using the initial conditions and the ideal gas law.

$$n = \frac{(1.0 \text{ atm}) (0.780 \text{ L})}{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) (298 \text{ K})} = 3.19 \times 10^{-2} \text{ mol}$$

The problem can be solved by breaking down the process into 2 steps: (1) isothermal expansion from 0.780 L at 1.0 atm to 1.25 L. The temperature is kept at 20°C; (2) heating at constant volume (1.25 L) from 25°C to 85°C. The entropy changes for these two steps, ΔS_1 and ΔS_2 are

$$\begin{aligned} \Delta S_1 &= nR \ln \frac{V_2}{V_1} = (3.19 \times 10^{-2} \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{1.25 \text{ L}}{0.780 \text{ L}} = 0.125 \text{ J K}^{-1} \\ \Delta S_2 &= C_V \ln \frac{T_2}{T_1} = \frac{3}{2} nR \ln \frac{T_2}{T_1} = \frac{3}{2} (3.19 \times 10^{-2} \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{358 \text{ K}}{298 \text{ K}} \\ &= 7.30 \times 10^{-2} \text{ J K}^{-1} \end{aligned}$$

The entropy change for the entire process is

$$\Delta S = \Delta S_1 + \Delta S_2 = 0.125 \text{ J K}^{-1} + 7.30 \times 10^{-2} \text{ J K}^{-1} = 0.20 \text{ J K}^{-1}$$

5.47 In the reversible adiabatic expansion of an ideal gas, there are two contributions to entropy changes: the expansion of the gas and the cooling of the gas. Show that these two contributions are equal in magnitude but opposite in sign. Show also that for an irreversible adiabatic gas expansion, these two contributions are no longer equal in magnitude. Predict the sign of ΔS .

A reversible adiabatic expansion process can be broken down into 2 steps: (1) isothermal expansion at T_1 from V_1 to V_2 , and (2) constant volume cooling at V_2 from T_1 to T_2 . The entropy changes for these 2 steps are

$$\Delta S_1 = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_2 = C_v \ln \frac{T_2}{T_1}$$

For a reversible adiabatic process,

$$\left(\frac{V_1}{V_2}\right)^{\gamma-1} = \frac{T_2}{T_1}$$

Therefore,

$$\begin{aligned} \Delta S_2 &= C_v \ln \left(\frac{V_1}{V_2}\right)^{\gamma-1} = C_v (\gamma - 1) \ln \frac{V_1}{V_2} = C_v \left(\frac{C_p}{C_v} - 1\right) \ln \frac{V_1}{V_2} = (C_p - C_v) \ln \frac{V_1}{V_2} \\ &= nR \ln \frac{V_1}{V_2} = -\Delta S_1 \end{aligned}$$

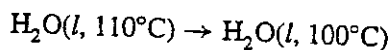
The contributions from the 2 steps are equal in magnitude but opposite in sign. As a result, the overall change in entropy is 0.

In an irreversible expansion between the same two volumes, less work is done by the system than in the reversible case. Since the expansion is adiabatic, $q = 0$ and $\Delta U = w$. Thus, the internal energy of the gas suffers a smaller decrease in the irreversible expansion. For an ideal gas, $\Delta U = C_v \Delta T$ so that the temperature difference is smaller, or $T_2^{\text{irrev}} > T_2^{\text{rev}}$. This means that in the irreversible expansion ΔS_2 is not as negative as for the reversible case, and $\Delta S > 0$.

5.49 Superheated water is water heated above 100°C without boiling. As for supercooled water (see Example 5.7), superheated water is thermodynamically unstable. Calculate the values of ΔS_{sys} , ΔS_{surr} , and ΔS_{univ} when 1.5 moles of superheated water at 110°C and 1.0 atm are converted to steam at the same temperature and pressure. (The molar enthalpy of vaporization of water is 40.79 kJ mol⁻¹, and the molar heat capacities of water and steam in the temperature range 100-110°C are 75.5 J K⁻¹ mol⁻¹ and 34.4 J K⁻¹ mol⁻¹, respectively.)

The entire process can be broken down into 3 steps: (1) cooling of H₂O(l) from 110°C to 100°C; (2) supplying heat to system to effect the phase transformation of H₂O from liquid to gas at 100°C; and (3) heating H₂O(g) from 100°C to 110°C.

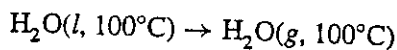
Step 1



$$\Delta S_1 = C_p \ln \frac{373 \text{ K}}{383 \text{ K}} = (1.5 \text{ mol}) (75.5 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{373 \text{ K}}{383 \text{ K}} = -3.00 \text{ J K}^{-1}$$

$$q_{\text{surr},1} = -q_1 = -C_p \Delta T = -(1.5 \text{ mol}) (75.5 \text{ J K}^{-1} \text{ mol}^{-1}) (373 \text{ K} - 383 \text{ K}) = 1.13 \times 10^3 \text{ J}$$

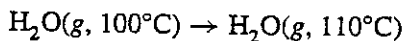
Step 2



$$\Delta S_2 = \frac{\Delta H_{\text{vap}}}{T_b} = \frac{(1.5 \text{ mol}) (40.79 \times 10^3 \text{ J mol}^{-1})}{373 \text{ K}} = 164 \text{ J K}^{-1}$$

$$q_{\text{surr},2} = -q_2 = -\Delta H_{\text{vap}} = -(1.5 \text{ mol}) (40.79 \times 10^3 \text{ J mol}^{-1}) = -6.12 \times 10^4 \text{ J}$$

Step 3



$$\Delta S_3 = C_p \ln \frac{383 \text{ K}}{373 \text{ K}} = (1.5 \text{ mol}) (34.4 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{383 \text{ K}}{373 \text{ K}} = 1.37 \text{ J K}^{-1}$$

$$q_{\text{surr},3} = -q_3 = -C_p \Delta T = -(1.5 \text{ mol}) (34.4 \text{ J K}^{-1} \text{ mol}^{-1}) (383 \text{ K} - 373 \text{ K}) = -516 \text{ J}$$

Therefore, for the entire process,

$$\Delta S = -3.00 \text{ J K}^{-1} + 164 \text{ J K}^{-1} + 1.37 \text{ J K}^{-1} = 162 \text{ J K}^{-1}$$

$$q_{\text{surr}} = 1.13 \times 10^3 \text{ J} - 6.12 \times 10^4 \text{ J} - 516 \text{ J} = -6.06 \times 10^4 \text{ J}$$

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} = \frac{-6.06 \times 10^4 \text{ J}}{383 \text{ K}} = -158 \text{ J K}^{-1}$$

$$\Delta S_{\text{univ}} = 162 \text{ J K}^{-1} - 158 \text{ J K}^{-1} = 4 \text{ J K}^{-1}$$

$\Delta S_{\text{univ}} > 0$ confirms the expectation that superheated water vaporizes spontaneously.