Homework Set #2 solutions   September 12, 2001

From Atkins: 2.8, 2.15, 2.16, 2.17, 2.18, 2.21, 2.23, 2.26

2.8) A sample of methane of mass 4.50 g occupies 12.7 L at 310 K. (a) Calculate the work done when the gas expands isothermally against a constant external pressure of 200 Torr until its volume has increased by 3.3 L. (b) Calculate the work that would be done if the same expansion occurred isothermally and reversibly.

(a) For an expansion against constant pressure, $w = -p_{ex} \Delta V$,

$$w = -(200 \text{ Torr})(3.3 \text{ L}) = -660 \text{ Torr L}$$

$$-660 \text{ Torr L} \times \frac{133.32 \text{ Pa}}{\text{Torr}} \times \frac{1 \text{ dm}^3}{\text{L}} \times \left(\frac{1 \text{ m}}{10 \text{ dm}}\right)^3 = -88 \text{ J}$$

(b) For an isothermal, reversible expansion of a perfect gas: $w = -nRT \ln \dfrac{V_f}{V_i}$,

$$n = \frac{4.50 \text{ g}}{16.042 \text{ g}/\text{mol}} = 0.28051 \text{ moles}$$

$$w = -(0.28051)(8.31451)(310 \text{ K}) \ln \frac{12.7 + 3.3}{12.7} = -167 \text{ J}$$

Note that you get more work out of a reversible process!

2.15) When 229 J of energy is supplied as heat to 3.00 mol Ar(g) at a constant volume, the temperature of the sample increases by 2.55 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

at constant <u>volume</u>:

$$q = q_v = C_v \Delta T = nC_{v,m} \Delta T$$

$$C_{v,m} = \frac{q_v}{n\Delta T} = \frac{229 \text{ J}}{(3.00)(2.55 \text{ K})} = 29.9 \text{ J mol}^{-1} \text{ K}^{-1}$$

Remember that $C_{p,m} - C_{v,m} = R$, (perfect gas only)

$$\text{so } C_{p,m} = C_{v,m} + R$$
$$= 29.9 + 8.31451$$
$$= 38.2 \text{ J mol}^{-1} \text{ K}^{-1}$$

2.16) The heat capacity of air at room temperature and pressure is approximately

21 J K^{-1} mol^{-1}. How much energy is required to raise the temperature of a room

of dimensions 5.5m x 6.5m x 3.0m by 10°C? If losses are neglected, how long

will it take a heater rated at 1.5 kW to achieve that increase given that

1 W = 1 J s^{-1}?

The volume of the room is: (5.5m)(6.5m)(3.0m) = 107.25 m^3

Standard ambient temperature and pressure is 25°C (298.15 K) and 1 bar (10^5 Pa)

First calculate the # moles of air in the room:

$$n = \frac{pV}{RT} = \frac{(10^5 \text{ Pa})(107.25 \text{ m}^3)}{(8.31451)(298.15 \text{ K})} = 4326.4 \text{ moles}$$

then: $q = nC_{p,m}\Delta T = (4326.4)(21 \text{ J K}^{-1} \text{ mol}^{-1})(10°) = 908.5 \times 10^3 \text{ J}$
        $= 910 \text{ kJ}$

at 1.5 kJ/s: $908.5 \text{ kJ} \times \frac{1 \text{ s}}{1.5 \text{ kJ}} = 605.7 \text{ s} \approx 610 \text{ s}$

2.17) A sample of food was burned in an oxygen atmosphere and the temperature rose

by 2.89°C. When a current of 1.27 A from a 12.5 V source flowed through the

same calorimeter for 157 s, the temperature rose by 3.88°C. What is the heat

released by the combustion?

First find the heat capacity of the calorimeter:

$q = IVt = (1.27 \text{ A})(12.5 \text{ V})(157 \text{ s}) = 2492.4 \text{ J}$

$C = \frac{q}{\Delta T} = \frac{2492.4}{3.88°} = 642.4 \text{ J deg}^{-1}$

Then for our unknown sample, $q = C\Delta T = (642.4)(2.89°) = 1857 \text{ J} = 1.86 \text{ kJ}$

2.18) Calculate the heat needed to be supplied to a parcel of air containing 1.00 mol air molecules to maintain its temperature at 300 K when it expands reversibly and isothermally from 22.0 L to 30.0 L as it ascends.

For a perfect gas, $\Delta U = 0$, so from the 1st law of thermodynamics, $q = -w$

$$q = -w = nRT \ln \frac{V_f}{V_i} = (1.00)(8.31451)(300) \ln \frac{30.0}{22.0} \qquad \text{(rev, isotherm., perf.)}$$

$$= 773.6 \text{ J} = 774 \text{ J}$$

2.21) (a) Calculate the difference between the molar enthalpy and the molar internal energy of carbon dioxide regarded as a perfect gas at 298.15 K. (b) Is the molar enthalpy increased or decreased when intermolecular forces are taken into account? For the latter calculation, treat carbon dioxide as a van der Waals gas and use the data in Table 1.5.

(a) $H = U + pV$, so for a perfect gas $H = U + nRT$ and $H_m = U_m + RT$

$$H_m - U_m = RT = (8.31451)(298.15) = 2479.0 \text{ J mol}^{-1}$$

(b) for a van der Waals gas, $p = \dfrac{RT}{V_m - b} - a\left(\dfrac{1}{V_m}\right)^2$

So, how does pV_m differ between a van der Waals gas and a perfect gas (where it equals RT) ? There are probably a few different ways to get at this question, but for a given pressure we can simplify this by looking then just at the molar volume, V_m. Rearranging the van der Waals eqn.:

$$V_m = \frac{RT}{p + \dfrac{a}{V_m^2}} + b \qquad\qquad (1)$$

where for CO_2, a=3.59 L^2 atm mol^{-2}, b=0.043 L mol^{-1}

While we can't solve this directly, we can use the method of successive approximations. For a perfect gas, $V_m = \dfrac{RT}{p} = \dfrac{(0.0820578)(298.15)}{1 \text{ atm}} = 24.4655 \text{ L}$

Substituting this value in as an initial guess into eqn.(1):

$$V_m \cong \frac{24.4655}{1 + \dfrac{3.59}{(24.4655)^2}} + 0.043 = 24.3626 \text{ L}$$

Substituting this new value back into (1):

$$V_m \cong \frac{24.3626}{1 + \dfrac{3.59}{(24.3626)^2}} + 0.043 = 24.3614 \text{ L}$$

on comparison we see we are converged to sufficient accuracy to say that

pV_m (vdW) $< pV_m$ (perfect) and hence that the molar enthalpy decreases when

intermolecular interactions are included in the case of CO_2.

2.23) When 3.0 mol of $O_2(g)$ is heated at a constant pressure of 3.25 atm, its

temperature increases from 260 K to 285 K. Given that the molar heat capacity of

O_2 at constant pressure is 29.4 J K^{-1} mol^{-1}, calculate q, ΔH, and ΔU.

a) at constant pressure, $q = nC_{p,m}\Delta T = (3.0)(29.4)(25) = 2205 \text{ J} = 2.2 \text{ kJ}$

b) since we're at constant pressure, $\Delta H = q = 2.2 \text{ kJ}$

c) $\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T$ (perfect gas)

$\Delta U = \Delta H - nR\Delta T$

$= 2205 - (3.0)(8.31451)(25)$

$= 1581 \text{ J}$

$= 1.6 \text{ kJ}$

2.26) The heat capacity of a substance is often reported in the form

$$C_{p,m} = a + bT + \frac{c}{T^2}$$

Use this expression to make a more accurate estimate of the change in molar enthalpy of carbon dioxide when it is heated from 15°C to 37°C given $a = 44.22$ J K^{-1} mol^{-1}, $b = 8.79$ x 10^{-3} J K^{-2} mol^{-1}, and $c = -8.62$ x 10^5 J K mol^{-1}.

For infinitessimal temperature changes: $dH = C_p dT$, or $dH_m = C_{p,m} dT$

Finite changes ($T = 288.15$ K to 310.15 K) are then given by:

$$\Delta H_m = \int_{T_i}^{T_f} C_{p,m} dT = \int_{T_i}^{T_f} \left(a + bT + \frac{c}{T^2} \right) dT$$

$$= \left(aT + \frac{b}{2}T^2 - \frac{c}{T} \right) \Big|_{T_i}^{T_f}$$

$$= a(T_f - T_i) + \frac{b}{2}\left(T_f^2 - T_i^2 \right) - c\left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$= a(22) + \frac{b}{2}(13162.6) - c\left(\frac{1}{310.15} - \frac{1}{288.15} \right)$$

$$= 818 \text{ J mol}^{-1}$$