Answers to assigned problems in Engel and Reid

Assignment # 1

Q1.1 copper > concrete > cork > vacuum

Q1.6 open, closed

Q1.7 modified (i) a movable adiabatic wall, (ii) a rigid fixed wall made of a heat conducting material like copper

P1.4 $O_2 : 0.517, CO_2 : 0.207, H_2O : 0.276$. The balanced rxn is $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$, the no. of moles before the rxn are 1, 12.5, 0, and 0; after the rxn they are 0, 7.5, 3, and 4.

P1.8 29.7 L. We have 0.0500 mol of water. The pressure of gaseous water at that T is 0.04187 atm. $P\Delta V = RT\Delta n$, where Δn is the change in no. of moles of water in gas form.

P1.12 403×10^3 Pa

P1.14 0.373 mol/min. no. of moles of gas inhaled per minute is $40 \times PV/RT = 6.54$ mol. 0.50% of that, 0.0327 mol, is water vapor. The exhaled air has the same V but 6.2/0.5=12.4 times more water vapor in it, 0.406 mol. The difference is $0.406 - 0.0327 = 0.373$ mol/min.

Assignment # 2

Q2.2 $P_f = T_f(nR/V_f)$. We are told (nR/V_f) is the same in both cases. In a adiabatic expansion $q = 0$, $w < 0$, therefore $\Delta U < 0$ and for a I.G. (and even a real gas), T goes down. So $T_f(adiabatic) < T_f(isothermal)$ and $P_f(adiabatic) < P_f(isothermal)$.

Q2.5 No. (1) q_p is a special case of q where the path has been specified; and (2) even then, q_p is the *difference* between two values of a state function at *two different times* and that's not a state function.

Q2.6 $w < 0$ (it expands as it turns from liquid to gas), $\Delta U > 0$ bc T is going up, $\Delta U = q + w$ so we must have $q > 0$ (but that was clear anyway: that's what a microwave oven does to water!).

Q2.7 System II is NOT a "single phase system of constant composition", far from it! So it's entirely possible that its T goes up even as its U goes down. Recall there's a close connection between T and the kinetic energy (KE) of molecules; U relates to KE plus PE (potential energy of molecules). So, if PE goes down a lot, it's possible that KE (and T) goes up a little and U still goes down. In this example, PE goes down as the atoms in the combustion rxn rearrange into more stable products.

Q2.13 No, we can't say.

P2.2 $q = 0, \Delta U = (3/2)Rn\Delta T = 1297J, w = 1297J, \Delta H = \Delta U + nR\Delta T = 2162J$.

P2.6 a) -4400 J, b) -5720 J. $\Delta V = 44.0L = 0.044m^3$. a) At constant P, $w = -P_{ext}\Delta V$. b) for isothermal rev. expansion, use Eq.(2.38).

P2.7 $q = 0$ (adiabatic). $C_{pm} = C_{vm} + R = 5R/2$ and $\gamma = 5/3$, so $T_f = T_i(V_f/V_i)^{1-5/3} = 156.85K$. $w = C_V\Delta T = -2946J$. $\Delta H = \Delta U + nR\Delta T = -4910J$.

P2.9 $w = -P_{ext}\Delta V = -0.196J$. Assume C_{pm} is constant over the T range: $q = nC_{pm}\Delta T = 39742J$. $|w| \ll q, \Delta U = q$. P is constant so $\Delta PV = -w \approx 0, \Delta H = 39.7kJ$.

Assignment # 3

P2.14 It's a long problem. First let's find out P, T, V for initial and final conditions

	n	P (bar)	T (K)	V (m^3)
initial	2.75	4.75	375	0.01805(1)
final a)	2.75	1.00	375(2)	0.085743(3)
final b)	2.75	1.00	201.1(5)	0.045972(4)

(1) $V = nRT/P$
(2) bc "isothermal"
(3) $V = nRT/P$
(4) see section 2.10, we use $P_i V_i^\gamma = P_f V_f^\gamma$.
$\gamma = C_P/C_V = 5/3$ for a I.G.
$V_f = V_i \ (P_i/P_f)^{1/\gamma} = 0.045972$
(5) $T = PV/nR = 201.059\,K$
For case a): $w = -nRT\ln(V_f/V_i) = -13361\,J$
For case b): $w = \Delta U - q = \Delta U = (3/2)nR\Delta T = -5964\,J$
c) When a gas expands $w < 0$ so $T \searrow$. If the expansion is *not* adiabatic, heat flows into the bas bc of the different $T_{system} - T_{surroundings} < 0$. As heat flows into the gas, $T \nearrow$ and since $PV = nRT$, P and/or V increase: either way this will bring additional expansion (more negative work).

P2.21 $\Delta H = n\int_{T_i}^{T_f} C_{P,m} dT$
$= 3.25 \times [44.35(300 - 750) + (1/2)0.00147(300^2 - 750^2)] = -66.0\,kJ$.

P2.25 $KE = mv^2/2 = 191.0\,J$
$\Delta T = q/C = 191.0\,J/(2.0\,J\,g^{-1}\,K^{-1} \cdot 220\,g) = 0.43\,K$

P2.38 $\Delta V = 0$ so $w = 0$, $q = \Delta U = C_v\Delta T = 20.8 \times 2.50 \times 294.5 = 15314\,J$
$\Delta H = \Delta U + nR\Delta T = 21436\,J$.

additional question: all these cases involve a gas (system) entirely surrounded by another gas, and expanding quickly. Gases do not conduct heat quickly. So if the system-surroudings interface is gas-gas, and the process is fast, there is essentially no heat exchange between system and surroundings during that process (not enough time for heat exchange to take place to any significant degree).

Assignment # 4

Q3.3 Ethene C_2H_2 has more atoms than CO, more degrees of freedom (d.o.f.), and therefore, more ways to accomodate energy into KE of its constituent atoms. $\Delta T \sim KE \div$ no. of d.o.f.; $C_v \sim d(KE)/dT$ assuming heat all goes into a change of KE; $C_V \propto$ no. of d.o.f.

Q3.5 Let $N =$ no. of d.o.f., and see discussion in Q3.3
For Ar $N = 3$. To a rough approximation, for ethane $N = 3 \times 8 = 24$. However, chemical bonds in ethane put restrictions on the motion of its 8 atoms, so its effective N is less than 24 at low T. In the limit of extremely high T, the ethane molecule would break into 8 separated atoms and we get $N = 24$ again. The qualitative conclusion is this: in ethane, the *effective* number of degrees of freedom $N \leq 24$, and N increases with T (up to a limiting value of 24).

Q3.6 $\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T$
On the r.h.s., the 1st term is zero for a I.G. bc U depends only on T; the 2nd term is zero bc $PV = nRT$, and we have constant n, R, and T. So $\left(\frac{\partial H}{\partial P}\right)_T = 0$for a I.G. Real gases differ only slightly from I.G., so we can expect $\left(\frac{\partial H}{\partial P}\right)_T$ to be small for real gases.

Q3.8 For a I.G., the potential energy (PE) is flat (zero) as a funtion of intermolecular distance, ie, it is flat as a function of volume: $d(PE)/dV = 0$. The kinetic energy KE of I.G. depends only on T, so $d(KE)/dV = 0$. So $dU/dV = 0$ for a I.G., or more precisely $\left(\frac{\partial U}{\partial V}\right)_T = 0$. Real gases are similar to a I.G. in that respect bc the typical intermolecular distances in a gas at normal pressure and temperature is roughly 10–20Å, that is a large enough distance that the PE in that part of the curve is essentially flat, so $d(PE)/dV \approx 0$.

Q3.11 intensive: T, P
extensive: V, q, w, U, H

Assignment # 5

P3.6 $P_f = 48.9\, bar$.
Assume V_i is exactly 1 L for both water and the vessel's interior. Use the β for water and for the vessel to calculate the hypothetical volume change if they were two separate things:
$V_{water} = 1\,L + 1\,L \times (2.04 \times 10^{-4} \times 57.9) = 1.01181\,L$.
$V_{vessel} = 1\,L + 1\,L \times (1.66 \times 10^{-4} \times 57.9) = 1.00961\,L$.
But they are not separate things: the water fills that vessel, so the two volumes must be equal to each other; and they must both be $1.00961\,L$ because the vessel is rigid and water isn't (the κ of the vessel is assumed to be infinitely bigger than the κ of water). So water gets compressed:
$\kappa = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)$ and $\kappa^{-1} = -V\left(\frac{\partial P}{\partial V}\right) = (4.59 \times 10^{-5} bar^{-1})^{-1} = -21786\, bar$.
$V\left(\frac{\partial P}{\partial V}\right) = 21786 = 1.00\,L \times \left(\frac{dP}{1.011811 - 1.00961}\right)$: solving that gives $dP = 47.93\, bar$, so $P_f = P_i + dP = 1\, bar + 47.93\, bar = 48.93\, bar$.

P3.11 $T_f = 303.3\,K$.
$C(Au) = (67.0\, g/196.97\, g/mol) \times 25.4\, JK^{-1}mol^{-1} = 8.640\, J/K$
$C(water) = (165.0\, g/18.015\, g/mol) \times 75.3\, JK^{-1}mol^{-1} = 689.7\, J/K$
All heat lost by gold is gained by water, so
$q_{water} = -q_{gold} \quad ; \quad C_w \Delta T_w = -C_g \Delta T_g \quad ;$
$C_w(T_f - T_{w,i}) = -C_g(T_f - T_{g,i}) \quad ; \quad T_f(C_w + C_g) = C_g T_{g,i} + C_w T_{w,i}$
$T_f = \frac{C_g T_{g,i} + C_w T_{w,i}}{(C_w + C_g)} = 303.3\,K$.

P3.12 $w = -7.47\, kJ$ (note: $-6.55\, kJ$ is inaccurate), $q = \Delta H = 80.16\, kJ$, $\Delta U = 72.69\, kJ$.
We break down the calculation in 3 parts:

(1) heat required to vaporize 1.75 mol water at 373 K:
$q_{vap} = 1.75\, mol \times 40.7\, kJ/mol = 71.225\, kJ$, the $40.7\, kJ/mol$ was taken from another textbook.
(2) heat up the water vapor from 373 to 575 K:
$q = 1.75 \times 33.58\, JK^{-1}mol^{-1} \times (525 - 373)\, K = 8.932\, kJ$.
(3) PV work done by the water:
$w = -P_{ext}(V_f - V_i) = -1\, bar \times (0.06545\, m^3 - 3.31 \times 10^{-5}\, m^3) = -6.55\, kJ$.
This was obtained using $V_f = 1.75 \times 3.74 \times 10^{-2}$, ie, using the molar volume at 460 K. A better way is to estimate the molar volume at 525 K by extrapolation:
$V_m(525) \approx V_m(460) + \frac{V_m(460)-V_m(373)}{(460-373)} \times (525 - 460) = 4.27 \times 10^{-2}\, m^3$.
With this better value of V_m we get $V_f = 0.074725\, m^3 \quad , \quad w = -7.47\, kJ$.
Note: For a I.G. $V_m = RT/P$ so, at constant P, it makes sense to estimate $V_m(525)$ by linear extrapolation w.r.t. temperature.

P3.17 We use $(\partial P/\partial T)_V = \beta/\kappa$. For 1 mole of a I.G. $P = RT/V_m$ and $(\partial P/\partial T)_V = R/V_m$, so $R/V_m = \beta/\kappa$ and $\beta = R\kappa/V_m$.
For 1 mole of a vdW gas $P = RT/(V_m - b) - a/V_m^2$, $(\partial P/\partial T)_V = R/(V_m - b)$ and $\beta = R\kappa/(V_m - b)$.

P3.19 By definition, internal pressure is $(\partial U/\partial V)_T$. We need equation (3.19):
$(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$
$(\partial P/\partial T)_V = \frac{\partial}{\partial T}\left[\left(\frac{RT}{V_m-b} - \frac{a}{TV_m^2}\right)\right] = \left(\frac{R}{V_m-b} + \frac{a}{T^2V_m^2}\right)$
Substitute that in Eq. (3.19) gives
$(\partial U/\partial V)_T = \frac{RT}{V_m-b} + \frac{a}{TV_m^2} - P$

P3.34 $\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial(U+PV)}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial(PV)}{\partial T}\right)_V = C_V + V\left(\frac{\partial P}{\partial T}\right)_V$
By the chain rule
$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$ If we rearrange it we get
$\left(\frac{\partial P}{\partial T}\right)_V = \frac{-(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = (V\beta/V\kappa)$ so $\left(\frac{\partial H}{\partial T}\right)_V = C_V + V(\beta/\kappa)$

Assignment # 6

P4.2 -45.98 kJ/mol.
$\Delta(\Delta H_{rxn}) = \Delta C_{P,rxn} \Delta T = R(4.217 \times 2 - 3.466 \times 3 - 3.502)(300 - 1000) = 31813\, J/mol$. $\Delta H_{rxn}(300) = -123.77 + 31.81 = -91.96\, kJ/mol$, but this is for making 2 moles of NH_3, so divide by two.

P4.3 $\Delta H_f(K_2O) = -757.8\, kJ/mol.$
The rxn is $2K + \frac{1}{2}O_2 \rightarrow K_2O$. $C_{water} = 1450\, g \times 4.184\, J/(Kg) = 6066.8\, J/K$. For calorimeter plus water bath we have $C = (6066.8 + 1849) = 7916\, J/K$. $q = q_V = C\Delta T = 7916\, J/K \times 2.91\, K = 23035\, J$. The rxn gave off 23.035 kJ of heat for a number of moles of K(s) equal to $2.380/39.098 = 0.06087\, mol$. So we have $23.035 kJ/0.06087 mol = 378.43\, kJ/mol\ of\ \ K(s)$: we have twice as much per mole of K_2O, 757.8 kJ/mol, so $\Delta H_f(K_2O) = -757.8 kJ/mol$.
Note: the true $\Delta H_f(K_2O)$ is $-361.5\, kJ/mol$: it looks like there may be something wrong with the data given in the question.

P4.7 (a) take $C(g) + 4H(g) \rightarrow CH_4(g)$. $\Delta H_{rxn} = -74.6 - 716.7 - 4 \times 218.0 = -1663.3\, kJ/mol$. The C-H bond enthalpy is $\frac{1}{4} \times 1663.3 = 415.8\, kJ/mol$. Then: $\Delta U_{rxn} = -1663.3 - RT(-4) = -1653\, kJ/mol$, divide this by 4 to get the C-H bond energy: 413 kJ/mol.
parts (b) and (c) can be solved in the same way and with the result in 4.7(a) to get 4.7(b) and (c). (b) C-C bond energy is 330 kJ/mol. (c) The enthalpy for the CC double bond is 589.7 kJ/mol.

P4.14 $-59.8\, kJ/mol$.
Combine the 3 chemical equations given like this: $- + +$ to get a new reaction we call "A" with a $\Delta H = -572.4\, kJ/mol$. Then write the combustion reactions "B" and "C":
$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_{rxn} = -393.51\, kJ/mol.$
$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(\ell) \quad \Delta H_{rxn} = -1299.58\, kJ/mol.$
Now take the combinations $A + 2B - C$ to get $Ca(s) + 2C(s) \rightarrow CaC_2(s)$ and $\Delta H_f(CaC_2) = -572.4 + 2 \times (-393.51) - (-1299.58) = -59.8\, kJ/mol.$

P4.15 $C_{calorimeter} = 5716\, J/K.$

The no. of moles of benzoic acid is 1.35/122.1 = 0.011059. The combustion reaction is

$$C_6H_5COOH + \frac{15}{2}O_2(g) \rightarrow 7CO_2(g) + 3H_2O(\ell)$$

and it has $\Delta H_{rxn} = -285.8 \times 3 + (-393.5 \times 7) - 0 - (-385.2) = -3226.7\,kJ/mol$. Multiply this by 0.011059 to get $q_{rxn} = -35.683\,kJ$. The heat absorbed by water is $q_{water} = 1376 \times 4.184 \times 3.11 = 17905\,J$. Then the heat absorbed by the calorimeter is $q_{calorimeter} = 35683 - 17905 = 17778\,J = C_{calorimeter} \times 3.11$ which gives $C_{calorimeter} = 5716\,J/K$.

P4.30 The CH bond energy estimated by Pauling's formula is

$$\sqrt{432 \times 346} + 96.5 \times (2.55 - 2.20)^2 = 398.4\,kJ/mol$$

We estimate $\Delta U_{rxn} \approx 432 + 602 + (4-6) \times 398.4 - 346 = -108.9\,kJ/mol$. If instead we use the ΔH_f, we get

$$\Delta H_{rxn} = -84.0 - 0 - 52.4 = -136.4\,kJ/mol$$

$$\Delta U_{rxn} = \Delta H_{rxn} - RT(1-2) = -133.9\,kJ/mol$$

The % error on ΔU_{rxn} when we use bond energies instead of actual thermodynamic data (ΔH_f data) is

$(133.9 - 108.9)/133.9 = 19\%$.

Note: the second answer in the book (0%) was obtained by using a CH bond energy of 411 kJ/mol taken directly from Table 4.3. This gives $\Delta U_{rxn} \approx 432 + 602 + (4-6) \times 411 - 346 = -134.0\,kJ/mol$ which is almost exactly -133.9 (that's partly coincidental). Note also that the CH bond energy obtained for methane in P4.7a, 413 kJ/mol, is surely a better estimate of the CH bond energy in ethane and ethylene than what we get with Pauling's formula. With 413 kJ/mol we get:

$$\Delta U_{rxn} \approx 432 + 602 + (4-6) \times 413 - 346 = -138\,kJ/mol$$

This is a lot better than $-108.9\,kJ/mol$, but it is still in error by 3%. A few percent error is not unusual when estimating energies of reaction from bond energies: strictly speaking, the CH bond energy in methane is different from the CH bond energy in ethane; and both of these are different from the CH bond energy in ethene. So it's no surprise that energies of reactions calculated from bond energies are inexact.

Assignment # 7

Q5.6 The basic equation for change of entropy is $\Delta S = \int dq_{rev}/T$. To go from there to the equation given, we need to have: constant P (so that $q = \Delta H$); constant T (so that T can be "pulled outside" the integral); and the process should be reversible (so that $dq = dq_{rev}$).

Q5.9 Yes, and then No. There is no fuel in a refrigerator, energy comes from the surroundings (electricity). So, for the room as whole, U can only go up (I'm assuming the room is insulated from outside). There's no chemical reaction or other change in potential energy so, for the entire room, KE and the average temperature go up as a result of having the refrigerator plugged in.
Heat is leaving the refrigerator: that's what brings (and maintains) T down. That heat flows into the room (there's nothing to conduct heat to outside the house). The heat coming out of the refrigerator is at least equal to the heat loss in the interior of the refrigerator, in fact higher because there must be at least a little bit of friction in the mechanical parts of the refrigerator converting electrical work (the net energy input into the room) to heat. So looking at the refrigerator and its surroundings: $q > 0$. Opening the door of the refrigerator is not going to change that, it's only going to equilibrate the T between the interior of the refrigerator and outside. In the short term, opening the refrigerator will help as heat flows from the room to the inside of the refrigerator, so the room (excluding the refrigerator's interior) will cool down a bit. But in the long term, the refrigerator draws energy from outside the house (electric power), none of that energy does work, so it all goes as a net heat input into the room, and that will eventually warm up the room. So, if you don't care about what's in the refrigerator, you *can* cool down the room a *little bit* by opening the refrigerator and immediately disconnecting it.

Q5.10 It is smaller than the entropy of the dissolved solute: the matter (and energy) is less dispersed in a crystal than in a solute; also, the heat of crystallization is negative (atoms are in a lower potential energy configuration in the crystal than in solution, as it crystallizes the salt releases heat) so $dq_{rev}/T = dS$ is negative. A process where $\Delta S_{system} < 0$ is entirely possible, as long as $\Delta S_{system} + \Delta S_{surr.} \geq 0$.

Here $\Delta S_{surr.}$ is surely positive because heat is released by the salt as it crystallizes, which gets absorbed by the surroundings, so $q_{surr} > 0$.

Q5.14 (1) $\Delta S = 0$, no change because Ar atoms are indistinguishable from one another. (2) No, in that second case $\Delta S > 0$. One way to see that is treat the Ar and Ne separately: Ar expands to twice its original volume, its entropy goes up; Ne also expands to twice its original volume, its entropy goes up.

P5.2 a) $\epsilon = 1 - T_{cold}/T_{hot} = 1 - 303/813 = 0.627$.
b) $0.912 \times 0.467 \times 0.984 \times (1 - 0.05) = 0.398$.
c) Energy in one hour $= 3600 \times 355 \times 10^6\, J/s = 1.278 \times 10^{12}\, J$.
We need $(1.278 \times 10^{12}/29.0 \times 10^6 J/kg = 44069$ kg of coal *assuming 100% efficiency.* But the plant's efficiency is 0.398, so we need more coal:
$44069\, kg/0.398 = 110700\, kg = 110.7\, ton$ every hour.

P5.5 For that we'll need equation (5.24). We have 1 mol of water$= 18.016\, g$. The volume of that water: $0.018106\, kg \div 997\, kg\, m^{-3} = 1.807 \times 10^{-5}\, m^3$. For liquid water, $C_{Pm} = 75.3\, J\, K^{-1}\, mol^{-1}$ (see appendix). Putting it all together (with everything in SI units):
$\Delta S = 75.3 \times \ln(625/325) - 1.807 \times 10^{-5} \times 2.07 \times 10^{-4} \times (660 - 1.00) \times 10^5$
$= 49.24 - 0.246 = 49.0\, J\, K^{-1}$.

P5.19 a) $\Delta S_{tr} = \Delta H_{tr}/T_{tr} = 380\, J\, mol^{-1}/368.55\, K = 1.031\, J\, K^{-1}\, mol^{-1}$.
b) $\Delta S_{fusion} = \Delta H_{fusion}/T_{fusion} = 1230\, J\, mol^{-1}/392.15\, K = 3.136\, J\, K^{-1}\, mol^{-1}$.
c) multiply by 8 gives
$8.248\, J\, K^{-1}$ per mole of S_8 molecules and
$25.09\, J\, K^{-1}$ per mole of S_8 molecules.

Assignment # 8

P5.1 $\Delta S_{rxn}(298) = 6 \times 205.2 + 209.2 - 6 \times 70.0 - 6 \times 213.8 = -262.4\, J\, K^{-1}\, mol^{-1}$.
$\Delta H_{rxn}(298) = 2802.8\, kJ/mol$ calculated in a similar way, adding molar quanti-

ties for products and subtracting for reactants.
To get ΔS_{surr}: heat for the surroundings is the negative of heat for the system which is $q_P = \Delta H$.
$\Delta S_{surr} = q_{surr}/T_{surr} = -2802.8 \times 10^3\, J/mol \div 298\, K = -9405\, J\, K^{-1}\, mol^{-1}$
$\Delta S_{total} = -262.4 + (-9405) = -9.67 \times 10^3\, J\, K^{-1}\, mol^{-1}$.

$\Delta S = \int \frac{C_P\, dT}{T} \approx C_P \ln(T_2/T_1) = C_P \ln(330/298) = 0.102 \times C_P$
We could calculate the change of S for each of the 4 substances individually with that equation, but it's simpler to evaluate $\Delta C_{P,rxn}$ and then get
$\Delta(\Delta S_{rxn}) = \Delta C_{P,rxn} \times 0.102$
$\Delta(\Delta S_{rxn}) = 0.102 \times (-278.8) = -28.43$
$\Delta S_{rxn}(330K) = -262.4 - 28.43 = -290.8\, J\, K^{-1}\, mol^{-1}$.

P5.9 a) adiabatic means $q = 0$ and reversible means $q = q_{rev}$, so $q_{rev} = 0$ throughout the process, ie $dq_{rev} = 0$. But $dS = dq_{rev}/T$, therefore $dS = 0$ throughout the process, $\Delta S = 0$. Reversible implies $\Delta S_{total} = 0$; so $\Delta S_{surr} = \Delta S_{total} - \Delta S = 0$.
b) $P_{ext} = 0$ implies $w = 0$. The only way we could have $P_{ext} = 0$ is to have a vacuum surrounding the system. Then heat exchange between system and surroundings is also zero, $q = q_{surr} = 0$. From that we get $\Delta S_{surr} = 0$ and $\Delta U = 0$. Since $\Delta U = 0$, $\Delta T = 0$, and equation (5.18) becomes
$\Delta S = nR \ln(V_f/V_i) = (123g/28g/mol) \times 8.31451 \times \ln 4 = 50.6\, J\, K^{-1}$
$\Delta S_{total} = \Delta S + \Delta S_{surr} = 50.6\, J\, K^{-1}$.
c) isothermal tells us that
$\Delta S = nR \ln(V_f/V_i) = (123g/28g/mol) \times 8.31451 \times \ln 4 = 50.6\, J\, K^{-1}$
as before. "Reversible" tells us that $\Delta S_{total} = 0$. We get ΔS_{surr} by taking the difference: $-50.6\, J\, K^{-1}$.

P5.11 for a I.G., $\Delta U = (3/2)(nR\Delta T) = (3/2)(1.75 \times R \times (-400)) = -8730\, J$
$\Delta H = \Delta U + \Delta(PV) = (3/2)(nR\Delta T) + (nR\Delta T) = (5/2)(nR\Delta T) = -14550\, J$
$\Delta S = -nR \ln(P_f/P_i) + nC_{P,m} \ln(T_f/T_i) = -15.98 + (-27.72) = -43.7\, J/K$.

P5.13 We use equation (5.24) with $T_f = T_i$, so
$\Delta S = -V\beta(P_f - P_i)$

The volume for 1 mol Cu(s): $1 mol \times 63.55\, g/mol \div 8.92\, g/cm^3 = 7.124\, cm^3$.
First, assuming $\kappa = 0$:
$\Delta S = -7.124 \times 10^{-6}\, m^3 \times 0.492 \times 10^{-4}\, K^{-1} \times (1000 - 1) \times 10^5\, Pa = -0.035\, J/K$.
Now taking $\kappa = 0.76 \times 10^{-6}\, bar^{-1}$, we calculate the final volume:
$V_f = 7.124 \times 10^{-6}\, m^3 \times (1 - 0.76 \times 10^{-6}\, bar^{-1} \times 999\, bar) = 7.124 \times 10^{-6}\, m^3 \times 0.99924 = 7.1186 \times 10^{-6}\, m^3$.
The average volume over the process is $(1/2)(7.124 + 7.1186) \times 10^{-6}\, m^3 = 7.121 \times 10^{-6}\, m^3$. Using the average volume will change ΔS as follows:
$\Delta S = -0.035\, J/K \times (7.121/7.124) = -0.035\, J/K$: no change within the numerical accuracy.

P5.15 We assume the equation that is given can work for finite changes and write
$\Delta T = (T/C_P) \times (\Delta S + V\beta\Delta P)$
The process is reversible and adiabatic, therefore $q_{rev} = 0$ and $\Delta S = 0$. With SI units everywhere:
$\Delta T = (298/75.3) \times (0 + 0.018 \times 10^{-3} \times 2.04 \times 10^{-4} \times 999 \times 10^5) = -1.45\, K$
In the calculation we assumed that T was constant at $298\, K$, but T is obviously not constant, it goes from 298 to $296.4\, K$. We can refine our calculations by replacing $298\, K$ by the average temperature $(298 + 296.5)/2 = 297.3\, K$, and get $\Delta T = (297.3/298) \times (-1.452\, K) = -1.448\, K$. But that is still $-1.45\, K$ within our accuracy, so no real change.

P5.46 We need to calculate 3 contributions to ΔS separately with the same method as on page 97. Here's what we get:
1) $\Delta S_1 = 20.42\, J\, K^{-1}\, mol^{-1}$ in heating Pb(s) from 298 to $600.6\, K$.
2) $\Delta S_2 = 7.942\, J\, K^{-1}\, mol^{-1}$ for melting Pb(s) to Pb(ℓ) at $T = 600.6\, K$.
3) $\Delta S_3 = 13.00\, J\, K^{-1}\, mol^{-1}$ for heating Pb(ℓ) from 600.6 to $923\, K$
$\Delta S_1 + \Delta S_2 + \Delta S_3 = 41.36\, J\, K^{-1}\, mol^{-1}$ and $S^\circ(Pb(\ell, 923\, K) = 64.80 + 41.36 = 106.16\, J\, K^{-1}\, mol^{-1}$.

Assignment # 9

Q6.1 $\Delta H_{rxn} = 0$, see Eq. (6.77)

Q6.3 $\Delta n_{gas} = 0$, or in the unlikely case where $P = 1\,bar$ exactly (see (6.78)).

Q6.8 No bc P_{Ar} will always stay zero on the left. $P_{H_2,left} = P_{H_2,right}$

Q6.12 G, see page 118

Q6.13 *decreases* bc the system oppose the heat input by absorbing heat, ie by doing the reverse (endothermic) rxn. One can also use Eq. (6.77) to answer.

Q6.14 *increases* bc the system reacts in a way that partially offsets the increased total pressure of the rxn mixture, ie it reacts toward the side of the chemical equations with fewer gas molecules.

Q6.15 *decreases* bc Xe by itself does nothing to the rxn; however, keeping P constant while adding Xe surely implies that the partial pressures of all gases in the rxn mixture go *down*, which is just the opposite situations as in Q6.14.

Q6.16 *no change* bc the partial pressures of all gases in the rxn mixture are unchanged and Xe does not take part in the rxn.

Q6.17 *no change* bc a catalyst does not affect the position of the equilibrium, it only helps reach equilibrium faster: but we're already at equilibrium.

Q6.18 *decreases* bc the system will oppose the change, ie it will react to form O_2 (consumer CO_2).

P6.1 $\Delta H_{combustion} = -3268\,kJ/mol$
$\Delta S^\circ_{rxn} = -219.6$
$\Delta G^\circ_{rxn} = -3268 - 298 \times (-219.6)/1000 = -3202.6\,kJ/mol$
$\Delta H^\circ_{rxn} = \Delta U^\circ_{rxn} - T\Delta S^\circ_{rxn} = \Delta G^\circ_{rxn} - \Delta(PV) = \Delta G^\circ_{rxn} - RT\Delta n_{gas} = -3198.9\,kJ/mol.$

P6.5 (a) No bc calcite has the lower Gibbs free energy G.
(b,c) We have to find the difference in Gibbs free energy G at some higher pressure and see if aragonite becomes favored at some high enough P. We have
$dG = (\frac{\partial G}{\partial P})_T dP = VdP$
Compare 1 mol (100.08 g) of calcite to 1 mol aragonite:
calcite: $36.930\, cm^3$; aragonite: $34.157\, cm^3$
Let's see what happens if wee raise the pressure by 100 bar:
calcite: $\Delta G \approx VdP = 36.930 \times 10^{-6}\, m^3 \times 10^7\, Pa = 369.30\, J/mol$
aragonite: $\Delta G \approx VdP = 34.157 \times 10^{-6}\, m^3 \times 10^7\, Pa = 341.57\, J/mol$
The *difference* in G between calcite and aragonite *decreased* by $369.30 - 342.57 = 27.73 J/mol$. Clearly, if we keep increasing P, there will come a point where calcite and aragonite have the same G; and if we increase P further, calcite will spontaneously transform into aragonite. At 1 bar, the ΔG between calcite and aragonite is $1100\, J/mol$. In order to bring $\Delta G = 0$, we need a pressure much bigger than $100\, bar$, bigger by a factor (1100/27.73), so the pressure where transition occurs is
$P_{transition} = 1 + (1100/27.73) \times 100\, bar = 3968\, bar$.
d) No. $\Delta G = \Delta H - T\Delta S$ calcite has a higher entropy than aragonite, so increasing temperature will lower $T\Delta S$ (and G) more for calcite than for aragonite, it will increase the difference in G between the two.
P6.8 a) If ΔH and ΔS are constant w.r.t. T, then
$\Delta G_{denaturation}(303K) = 418kJ/mol - 303 \times 1.3 = 24.1kJ/mol$
b) $K = e^{-\Delta G^\circ_{rxn}/RT} = 7.0 \times 10^{-5}$.
c) yes, but at any given time 1 out of every 14,000 proteins is in a denatured form.

Assignment # 10

P6.10 $\Delta H^\circ_{rxn}(725K) = 35.2 \times 2 - (-19.5) = 85.9\, kJ/mol$.
$\Delta G^\circ_{rxn}(298K) = 51.3 \times 2 - 97.5 = 5.10kJ/mol$
$K_P(298K) = \exp(-5100/R298.15) = 0.1278$

$\ln K_P(725K) = \ln K_P(298K) - (\Delta H^\circ_{rxn}/R)(1/725 - 1/298) = 18.34$
$K_P(725K) = \exp(18.34) = 9.3 \times 10^7$
(there are other ways to solve and get to the same answer)

P6.11a $K_P = (.271)^2/(.229)^2 = 1.400$
$\Delta G^\circ_{rxn} = -RT \ln K_P = -2800\, J/mol$

P6.13 a) $P = P(H_2O) + P(CO_2) = 0.235$ and $P(H_2O) = P(CO_2)$, so $P(H_2O) = P(CO_2) = 0.235/2 = 0.1175\, bar$.
$K_P = 0.1175^2 = 1.38 \times 10^{-2}$.
b) At equilibrium, $K_P = P(H_2O) \cdot P(CO_2) = (0.105 + x) \cdot x = 0.0138$. Solving the quadratic and keeping the root $x > 0$ (x can't be negative the way I defined it) gives $x = P(CO_2) = 0.07617\, bar$.
Verify: $0.07617 \cdot (0.105 + 0.07617) = 0.0138$, as it should.

P6.15 a) $\Delta G^\circ_{rxn} = -80.3 + 0 - 0 - (3/2) \cdot (-237.1) = +275.35\, kJ/mol$
b) $K = \exp(-\Delta G^\circ_{rxn}/RT) = 5.8 \times 10^{-49}$.
c) No! ΔG°_{rxn} is very large positive; unless the concentration of $NH_3(aq)$ is *exceedingly small*, ΔG_{rxn} will be positive (we know that $P(O_2)$ is *not* exceedingly small).

P6.17 The convention in section 6.17 is that $H = 0$ for N_2: with that convention $G = -TS^\circ_m$ and we have
$\mu(N_2, 298K, x = 0.800) = -TS^\circ_m + RT \ln 0.800 = 298.15 \cdot (-191.6 + R \ln 0.8) = -57.68 kJ/mol$.
P6.22 $n = 6.89 mol$ (sum of the 3). The molar fractions of He, Ne, Ar are 0.450, 0.356, 0.194, and
$\Delta G_{mixing} = nRT \sum_i x_i \ln x_i = -20.96 kJ$
compare equations (6.47) and (6.49):
$\Delta S_{mixing} = -\Delta G_{mixing}/T = 59.9 J/K$

P6.36 a) shifts to the right (ozone formation) bc the system reacts in a way to decrease P (oppose the change)

b) shifts to the right to absorb (remove) some of the heat that went in when T was increased.
c) $\Delta G^\circ_{rxn} = 163.2 \times 2 - 0 = 326.4 kJ/mol$
$K_P(298K) = e^{-\Delta G^\circ_{rxn}/RT} = 6.15 \times 10^{-58}$ at 298 K. For 750 K we take
$K_P(750K) = \exp[\ln 6.15 \times 10^{-58} - (285400/R) \cdot (1/750 - 1/298) = 8.7 \times 10^{-28}$
d) $K_x = K_P(P/P^\circ)^{-\Delta n_{gas}} = 8.7 \times 10^{-28}(1.5)^1 = 1.3 \times 10^{-27}$.

Q9.13 Two liquids are immisicible is $\Delta G_{mixing} > 0$. $\Delta G = \Delta H - T\Delta S$. If $\Delta S_{mixing} > 0$ it contributes a negative $-T\Delta S_{mixing}$ to ΔG_{mixing}: the liquids would mix. But there is ΔH_{mixing} to consider also: if it is positive, and larger than $-T\Delta S_{mixing}$, the $\Delta G_{mixing} > 0$ and liquids will not mix. So, immiscibility is normally explained as resulting from a positive, and sufficiently large ΔH_{mixing}. Note however that ΔS_{mixing} is sometimes negative, for instance in aqueous solutions (that is the origin for the hydrophobic effect).

P9.8 $P_{benzene} = 0.33 \times 244\, torr = 80.52\, torr$.
$P_{hexane} = 0.67 \times 366\, torr = 245.22\, torr$.
$P_{total} = 80.52 + 245.22 = 325.7\, torr$.

Answers to Test # 1

1. +, 0, $-$

2. F, F, T

3. volume, energy

4. $n(H_2) = 40.34$, $n(Ar) = 57.61$, $V = 1.500$; 1.54×10^5 Pa

5. -2.50 kJ ; -3.55 kJ

6. 4 things:
to get ΔU you must integrate dU
$(\partial U/\partial T)_V = C_V$
for gases $(\partial U/\partial V)_T = 0$ (I.G.) or very small (real gases)
for liquids and solids, dV is small

7. many possible answers: κ is bigger for liquids; κ is unusually small for water (bc of H bonds); κ is unusually small for graphite (bc of stiff C-C bonds); κ of C_2H_5OH is different from κ of CH_3OCH_3 showing the importance of structure (and H bonds).

8. $\int_{T_i}^{T_f} C_p dT = [(250T + 7.5 \times 10^{-3} T^2/2)|_{500}^{300} = -50600$ J

Answers to Test # 2

1. $\Delta H_{rxn} = 227.4 + 3 \times 0 - 2 \times (-74.6) = 376.6\, kJ/mol$
We need $\Delta C_{P,rxn}$ to get ΔH_{rxn} at another T:
$\Delta C_{P,rxn} = 44.0 + 3 \times 28.8 - 2 \times 35.7 = 59.0\, J\, K^{-1}\, mol^{-1}$
$\Delta H_{rxn}(234\, K) = \Delta H_{rxn}(298\, K) + \Delta C_{P,rxn} \times (234 - 298) = 372.8\, kJ/mol$

2. $\Delta U_{rxn} =$ "bond energies of reactants" $-$ "bond energies of products" (e.g., in the **endothermic** reaction $H_2 \rightarrow 2H$ we **break** a bond).
$\Delta U_{rxn} = 432 \times 2 + 494 - 2 \times (2 \times D(OH))$ (2 water molecules and each has 2 OH bonds).
We must estimate $D(OH)$, otherwise we can't calculate a ΔU_{rxn}.
$D(OH) \approx \sqrt{432 \cdot 142} + 96.5 \cdot (3.44 - 2.20)^2 = 396.1$
$\Delta U_{rxn} = -226\, kJ/mol.$
$\Delta H_{rxn} = \Delta U_{rxn} + RT\Delta n_{gas} = \Delta U_{rxn} + RT \cdot (0 - 3) = -234\, kJ/mol$
Note: the true ΔH_{rxn} is $-572\, kJ/mol$; $-234\, kJ/mol$ is a very poor estimate but it is the best we can do with the data given. The large error is mostly due to the fact that $D(OH) \approx 396.1$ is a very poor estimate of the O-H bond energy: a better estimate of the O-H bond energy is $459\, kJ/mol$, see Table 4.3.

3. We have to do 4 things to go from equation (1) to (2): 1) integrate; 2) assume that the transition occurs reversibly; 3) assume that pressure is constant; 4) use the fact that T is constant during a transition.

4a. $\Delta S = 0$ bc the process is adiabatic ($q = 0$) and reversible ($q_{reversible} = 0$) which implies $dS = (1/T)dq_{rev} = 0$
4b. $\Delta S > 0$ bc isothermal implies $\Delta U = 0$ for a gas, and $w < 0$ (expansion), so $q > 0$, $q_{rev} > 0$.

5. $\epsilon = 1 - T_{cold}/T_{hot} = 1 - 298/373 = 0.201$

6a. We have to assume that $\frac{\Delta T}{\Delta P} \approx \left(\frac{\partial T}{\partial P}\right)_H$ otherwise we have no data to calculate anything. So

$\frac{\Delta T}{\Delta P} \approx 2.69 \times 10^{-6}$
$\Delta P = P_f - P_i \approx 1\,bar - 100\,bar = -99\,bar$ (the final pressure was not given, so we have to assume something: gas cylinders are normally kept in a "normal room" at P near 1 bar).
$\Delta T \approx 2.69 \times 10^{-6} \times (-99 \times 10^5)$ in SI units, $\Delta T \approx -26.6\,K$.
$T_{final} \approx 25 - 26.6 = -1.6$°C.

6b. H is roughly constant; U is roughly constant. But T is not related to H or U, it is related to kinetic energy (KE). Assume $\Delta U = 0$, so $0 = \Delta(KE) + \Delta(PE)$ where PE is the potential energy of the gas molecules. If T went down it means that KE went down; and if $\Delta U = 0$, that implies that the PE went up. That's entirely possible, no contradiction there.
Note: for a I.G. the PE is always zero and therefore the JT experiment produces no change of T (see the JT coefficients for He, Ne, Ar: they are all very small).