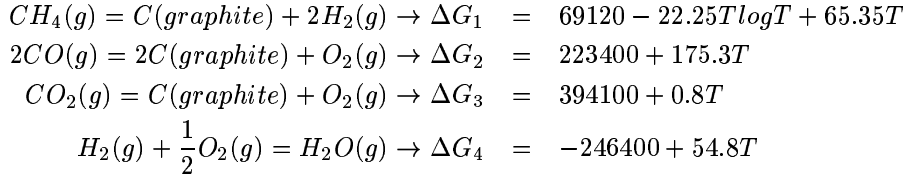


3.00 Thermodynamics Fall 2002  
Problem Set 6 Solutions

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**Solution 6.1**



The number of elements in the reaction = 3 (C, H, O) Number of gaseous components in the reactions = 6 ( $CO_2, CO, CH_4, H_2, O_2, H_2O$ , excluding graphite) The above reactions are the reactions at equilibrium and these can be arranged in any order. There are two ways to go about solving this problem. The first is easier. We examine the mole balance in the system. The system contains the species  $CO_2, CO, CH_4, H_2, O_2, H_2O$  (excluding graphite) and thus

$$n_C, \text{ the number of moles of C, } = n_{CH_4} + n_{CO_2} + n_{CO} \quad (1)$$

$$n_O, \text{ the number of moles of O, } = 2n_{CO_2} + n_{CO} + n_{H_2O} \quad (2)$$

$$n_H, \text{ the number of moles of H, } = 2n_{H_2} + 2n_{H_2O} + 4n_{CH_4} \quad (3)$$

Initially, 1 mole of  $CH_4$  was mixed with 1 mole of  $CO_2$ , and thus, in a closed system,

$$\frac{n_C}{n_O} = 1 \quad (4)$$

$$\frac{n_H}{n_O} = 2 \quad (5)$$

Using the above relations,

$$n_{H_2} + n_{H_2O} + 2n_{CH_4} = 2n_{CO_2} + n_{CO} + n_{H_2O} \quad (6)$$

or, as  $n_i \propto p_i$  at constant P,

$$p_{H_2} + 2p_{CH_4} = 2p_{CO_2} + p_{CO} \quad (7)$$

and also,

$$n_{CH_4} + n_{CO_2} + n_{CO} = 2n_{CO_2} + n_{CO} + n_{H_2O} \quad (8)$$

or

$$p_{CH_4} = p_{CO_2} + p_{H_2O} \quad (9)$$

In addition,

$$P = p_{CH_4} + p_{CO_2} + p_{CO} + p_{H_2} + p_{H_2O} \quad (10)$$

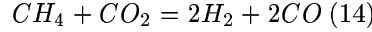
It is now possible to solve for  $p_{H_2}$ ,  $p_{H_2O}$ , and  $p_{CO}$  in terms of  $P$ , and  $p_{CH_4}$  and  $p_{CO_2}$  using Eqs. ??.

$$p_{H_2O} = p_{CH_4} - p_{CO_2} \quad (11)$$

$$p_{CO} = \frac{1}{2}P - p_{CO_2} \quad (12)$$

$$p_{H_2} = \frac{1}{2}P - 2p_{CH_4} + p_{CO_2} \quad (13)$$

The reaction (i) below has an associated change in Gibbs free energy of  $\Delta G_i^0$  and equilibrium reaction constant  $K_{p,i}$  at T=1750K.



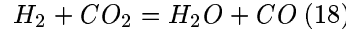
$$\Delta G_i^0 = 239820 - 22.25T \log T - 109.15T \text{ Joules} \quad (15)$$

$$K_{p,i} = \exp[-\Delta G_i^0(1750K, 1atm)/1750R] = \exp[241953/1750 * 8.314] = 16679009 \quad (16)$$

$K_{p,i}$  is related to the partial pressures of the gases by

$$K_{p,i} = \frac{p_{CO}^2 p_{H_2}^2}{p_{CO_2} p_{CH_4}} \quad (17)$$

And the following reaction (ii) has an associated change in Gibbs free energy of  $\Delta G_{ii}^0$  and equilibrium reaction constant  $K_{p,ii}$  at T=1750K.



$$\Delta G_{ii}^0 = 36000 - 32.05T \text{ Joules} \quad (19)$$

$$K_{p,ii} = \exp[-\Delta G_{ii}^0(1750K, 1atm)/1750R] = \exp[20088/1750 * 8.314] = 3711114 \quad (20)$$

$K_{p,ii}$  is related to the partial pressures of the gases by

$$K_{p,ii} = \frac{p_{CO} p_{H_2O}}{p_{CO_2} p_{H_2}} \quad (21)$$

The two equilibrium reaction constants,  $K_{p,i}$  and  $K_{p,ii}$  are related to the two independent variables,  $p_{CH_4}$  and  $p_{CO_2}$ , with  $P = 1atm$  as

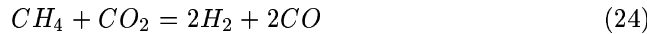
$$K_{p,i} = 16679009 = \frac{(\frac{1}{2}P - p_{CO_2})^2 (\frac{1}{2}P - 2p_{CH_4} + p_{CO_2})^2}{p_{CO_2} p_{CH_4}} \quad (22)$$

$$K_{p,ii} = 3711114 = \frac{(\frac{1}{2}P - p_{CO_2})(p_{CH_4} - p_{CO_2})}{p_{CO_2} (\frac{1}{2}P - 2p_{CH_4} + p_{CO_2})} \quad (23)$$

The simultaneous solution of these equations with P=1atm gives the solution to the problem.

Another way is presented below. (There are several ways to go about solving this problem, depending on the reactions that are chosen.)

Combining the first three reaction equations,



The standard free energy for the above equation is given by  $\Delta G_5 = \Delta G_1 + \Delta G_3 - \Delta G_2$ .

$$\Delta G_5 = \Delta G_1 + \Delta G_3 - \Delta G_2 = 77468.29J \quad (25)$$

$$4dn_{CH_4} + 2dn_{H_2} = 0 \quad (26)$$

$$2dn_{CO_2} + dn_{CO} = 0 \quad (27)$$

$$dn_{CH_4} + dn_{CO_2} + dn_{CO} = 0 \quad (28)$$

$$(29)$$

Since there are three equations with four variables, one independent variable can be identified, which we identify as  $x = dn_{CH_4}$ .

Reaction	$CH_4$	$CO_2$	→	$2H_2$	$2CO$
Initial	1	1	→	0	0
Equilibrium change	1-x	1-x	→	2x	2x

Combining reaction equations 2 and 3,

$$2CO_2 = 2CO + O_2 \quad (30)$$

The change in standard free energy is given by,

$$\Delta G_6 = 2\Delta G_3 - \Delta G_2 = 435825J \quad (31)$$

The constraints in the number of moles of components are,

$$2dn_{CO_2} + 2dn_{CO} + dn_{H_2O} = 0 \quad (32)$$

$$2dn_{H_2} + 2dn_{H_2O} = 0 \quad (33)$$

Reaction	$2CO_2$	→	$2CO$	$2O_2$
Initial	1-x	→	2x	0
Equilibrium change	1-x-2y	→	2x+2y	y

From the last reaction equation

$$H_2 + 1/2O_2 = H_2O \quad (34)$$

The change in the standard free energy (for T=1750K) is given in the problem statement as

$$\Delta G_4 = -246400 + 54.8 * 1750J = -150500J \quad (35)$$

The constraint equations are,

$$2dn_{H_2} + 2dn_{H_2O} = 0 \quad (36)$$

$$2dn_{O_2} + dn_{H_2O} = 0 \quad (37)$$

Reaction	$H_2$	$1/2 O_2$	→	$H_2O$
Initial	2x	y	→	0
Equilibrium change	2x-z	y-z/2	→	z

Thus at equilibrium, taking into account all the above reactions,

$$n_{CH_4} = 1 - x, n_{CO_2} = 1 - x - 2y, n_{H_2} = 2x - z, n_{CO} = 2x + 2y, n_{H_2O} = z, n_{O_2} = y - z/2 \text{ and } n_{tot} = 2 + 2x + y - z/2.$$

Thus, the partial pressures of the components,

$$P_{CH_4} = \frac{1-x}{(2+2x+y-z/2)}P \quad (38)$$

$$P_{CO_2} = \frac{1-x-2y}{(2+2x+y-z/2)}P \quad (39)$$

$$P_{H_2} = \frac{2x-z}{(2+2x+y-z/2)}P \quad (40)$$

$$P_{CO} = \frac{2x+2y}{(2+2x+y-z/2)}P \quad (41)$$

$$P_{H_2O} = \frac{z}{(2+2x+y-z/2)}P \quad (42)$$

$$P_{O_2} = \frac{y-z/2}{(2+2x+y-z/2)}P \quad (43)$$

Now we can list the partial pressures of the components.

If the reactions are at equilibrium, then the following relations hold.

$$\frac{P_{CO}^2 P_{H_2}^2}{P_{CH_4} P_{CO_2}} = \exp(\Delta G_{05}/RT)$$

$$\frac{(P_{CO})^2 P_{O_2}}{(P_{CO_2})^2} = \exp(\Delta G_{06}/RT)$$

$$\frac{P_{H_2O}}{P_{H_2} (P_{O_2})^{1/2}} = \exp(\Delta G_{04}/RT)$$

substituting the partial pressures of the individual components into the above equations,

$$\frac{2(x+y)^2(2x-z)P^2}{(1-x)(1-x-2y)(2+2x+y-z/2)^2} = 207.14 \quad (44)$$

$$\frac{(2x+2y)^2(y-z/2)P}{(1-x-2y)(2+2x+y-z/2)} = 1.06 * 10^{13} \quad (45)$$

$$\frac{z(2+2x+y-z/2)^{1/2}}{(2x-z)(y-z/2)^{1/2}} = 3.16 * 10^{-5} \quad (46)$$

$$(47)$$

There are three unknowns and three equations. In principle, it is possible to solve for the three unknowns simultaneously. The solution is not straightforward and some computational methodology need to be adapted for solving these simultaneous equations.

However with some simple approximations, an approximate analytical solution can be derived for the partial pressures. A first approximation would be to take RHS of eqn 23 to be zero. This would be give  $z = 0$  - and number of variables to be solved reduces to just  $x$  and  $y$ .

## Solution 6.2

The solution can be obtained through simple manipulations of Jacobian.

$$\left(\frac{\partial G}{\partial T}\right)_v = \frac{\partial(G, V)}{\partial(T, V)} \quad (48)$$

$$= \frac{\frac{\partial(G, V)}{\partial(T, P)}}{\frac{\partial(T, V)}{\partial(T, P)}} \quad (49)$$

$$= \frac{\left(\frac{\partial G}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T - \left(\frac{\partial G}{\partial P}\right)_T \left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} \quad (50)$$

Substituting for  $\left(\frac{\partial V}{\partial T}\right)_P$  and  $\left(\frac{\partial V}{\partial P}\right)_T$  in terms of  $\alpha$  and  $\kappa_T$ ,

$$\left(\frac{\partial G}{\partial T}\right)_v = \left(\frac{\partial G}{\partial T}\right)_P + \frac{1}{\left(\frac{\partial V}{\partial P}\right)_T} \left(\frac{\partial G}{\partial P}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad (51)$$

$$= -S + \frac{1}{V\kappa_T} V\alpha V \quad (52)$$

$$= -S + \frac{V\alpha}{\kappa} \quad (53)$$