# Exercises on Ch.3 Systems with variable composition

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# 3.1 Chemical potential

### Exercise 3.1.1

Derive an expression for  $\mu_j$  as a derivative of *S* instead of *U*.

### Hint

Use the entropy scheme.

# Solution

 $-dS = (-1/T)dU + (-P/T)dV + \Sigma(\mu_i/T)dN_i - (D/T)d\xi \text{ yields; } (\partial S/\partial N_i)_{U,V,N_{\kappa,\xi}} = -\mu_i/T.$ 

# Exercise 3.1.2

By  $\mu_j = (\partial U/\partial N_j)_{S,V,N\kappa}$  we mean a quantity evaluated under internal equilibrium, i.e. under the equilibrium value of  $\xi$  which varies with  $N_j$ . Show that this quantity has the same value as  $(\partial U/\partial N_j)_{S,V,N\kappa,\xi}$  with the equilibrium value of  $\xi$  inserted as a constant value.

# Hint

The kind of problem was treated in Section 2.2.

#### Solution

 $(\partial U/\partial N_j)_{S,V,N\kappa,eq} = (\partial U/\partial N_j)_{S,V,N\kappa,\xi} + (\partial U/\partial \xi)_{S,V,Ni} \cdot (\partial \xi/\partial N_j)_{S,V,N\kappa,eq}$ . However, at equilibrium  $(\partial U/\partial \xi)_{S,V,Ni} = -D = 0$  and thus  $(\partial U/\partial N_j)_{S,V,N\kappa,eq} = (\partial U/\partial N_j)_{S,V,N\kappa,\xi}$ .

## **3.2** Molar quantities

#### Exercise 3.2.1

Consider a real change in a system with a constant amount of one mole of atoms, N = 1. Formulate the combined law for that system.

#### Hint

Start from an ordinary form of the combined law and divide by N. Since N is constant, we get  $(1/N)dU = d(U/N) = dU_m$ , etc.

#### Solution

 $dU_{\rm m} = TdS_{\rm m} - PdV_{\rm m} + \Sigma\mu_{\rm i}dx_{\rm i} - Dd(\xi/N)$ 

## 3.3 More about characteristic state functions

#### Exercise 3.3.1

Express  $\mu_A$  in terms of molar quantities and insert the expression in the combined law for a pure element A.

#### Solution

 $\Sigma \mu_i x_i = G_m$  gives  $\mu_A = G_m$  (pure A). For pure A:  $dU = TdS - PdV + G_m dN$ .

# 3.5 Various forms of the combined law

#### Exercise 3.5.1

Formulate the Gibbs–Duhem relation based on the basic volume scheme. Then show that it is equivalent to the ordinary form.

#### Solution

 $Sd(T/P) + Ud(-1/P) + \Sigma N_i d(\mu_i/P) = 0; (S/P)dT - (TS/P^2)dP + (U/P^2)dP + \Sigma (N_i/P)d\mu_i - \Sigma (N_i\mu_i/P^2)dP = 0.$  Multiply by P and replace  $\Sigma N_i\mu_i$  by U + PV - TS:  $SdT - (TS/P)dP + (U/P)dP + \Sigma N_i d\mu_i - (U + PV - TS)/P \cdot dP = 0; SdT + \Sigma N_i d\mu_i - VdP = 0$ 

#### Exercise 3.5.2

Find the characteristic state function for the variables T/P, 1/T and  $N_i$ . Then change to T, P and  $N_i$  and check that the function changes to the Gibbs energy G.

# Hint

In order to replace  $dX^a$  by  $dY^a$ , subtract  $X^a Y^a$  from the characteristic state function.

## Solution

Line 8 in Table 3.1 yields  $d[(PV - U)/P] = -(1/T)d(TU/P) - (T/P)d(F/T) + \Sigma(\mu_i/P)dN_i$ . Subtract  $-(1/T)\cdot(TU/P) = -U/P$  and  $-(T/P)\cdot(F/T) = -F/P$  from (PV - U)/P:  $d[(PV - U + U + F)/P] = (TU/P)d(1/T) + (F/T)d(T/P) + \Sigma(\mu_i/P)dN_i$ . But (PV - U + U + F)/P = G/P. This is the new characteristic state function (for the independent variables T/P, 1/T and  $N_i$ ). Thus  $d(G/P) = (1/P)dG - (G/P^2)dP = -(TU/PT^2)dT + (F/TP)dT - (TF/TP^2)dP + \Sigma(\mu_i/P)dN_i$ ; i.e.  $dG = (1/P)dP \cdot (G - F) - (1/T)dT \cdot (U - F) + \Sigma\mu_i dN_i = VdP - SdT + \Sigma\mu_i dN_i$ .

## Exercise 3.5.3

Consider a solid system with no volatile components but in intimate contact with a large controllable volume of an ideal gas. The state of the system can be changed by altering its temperature and the volume of the gas,  $V_{g}$ . What characteristic state function would be the natural one to use?

### Hint

The ideal gas law relates some variables.

### Solution

At constant volume, the ideal gas will relate *T* and *P* by  $T/P = V_g/NR$  and the value of T/P will thus be controlled by the volume of the gas. The two state variables will thus be T/P and *T* or *P*. We find no such alternative in Table 3.1 but we find -1/T and -T/P on line 8. By changing variables in order to introduce the potentials as independent variables we get  $d[(PV - U)/P] - d[(-1/T) \cdot (TU/P)] - d[(-T/P) \cdot (F/T)] = -(TU/P)d(-1/T) - (F/T)d(-T/P) = d[V - U/P + U/P + F/P] = d(G/P)$ . We could also have started from line 2 in Table 3.1 with *T* and -P/T or line 4 with -1/T and -P/T.

# 3.8 Driving force for molecular reactions

### Exercise 3.8.1

Suppose one has evaluated an equilibrium constant K' for a gas reaction in terms of the mole fractions. How could one evaluate the driving force for the reaction from the set of initial values of the mole fractions?

### Hint

For an ideal gas mixture the partial pressures are defined from the mole fractions  $y_i$  by  $P_i = y_i P$ .

## Solution

$$K = \Pi(P_i)_{eq.}^{v_i} = P^{\Sigma v_i} \cdot \Pi(y_i)_{eq.}^{v_i} = P^{\Sigma v_i} \cdot K';$$
  
$$D = RT \ln[K / \Pi(P_i)^{v_i}] = RT \ln[P^{\Sigma v_i} K' / P^{\Sigma v_i} \Pi(y_i)^{v_i}] = RT \ln[K' / \Pi(y_i)^{v_i}]$$

# 3.9 Evaluation of integrated driving force as function of T or P

## Exercise 3.9.1

Consider 1 mole of a substance having a transformation point from  $\alpha$  to  $\beta$  at  $T_{\circ}$  under 1 bar. Use the relation  $dS = dQ/T + d_{ip}S$  to calculate the change of entropy at  $T_1 > T_{\circ}$  and 1 bar. Suppose  $\Delta H_{\rm m}$  and  $\Delta S_{\rm m}$  are independent of T.

## Hint

The internal entropy production is obtained from the driving force. The heat of reaction is equal to  $\Delta H_{\rm m}$  under constant *P*.

### Solution

 $\Delta_{ip}S = (1/T)\int Dd\xi = -\Delta G_m/T_1 = -\Delta H_m(T_o - T_1)/T_oT_1 = -\Delta H_m/T_1 + \Delta H_m/T_o; \ \Delta S = Q/T_1 + \Delta_{ip}S = \Delta H_m/T_1 - \Delta H_m/T_1 + \Delta H_m/T_o = \Delta H_m/T_o = \Delta S_m$  as one might have expected.

# 3.10 Effective driving force

### Exercise 3.10.1

Consider the mechanical device shown here. The left hand piston is supposed to have a friction against the cylinder, but not the right-hand piston. Between the two chambers there is a thin tube and the rate of transfer of gas from left to right is governed by the flow of gas through that tube. Examine how close an analogue this device would be to the example discussed in the text?



### Hint

Suppose the friction force is constant, i.e., independent of the rate of movement.

# Solution

If we compare  $P_0 - P_1$  with the chemical driving force and  $P_1 - P_2$  with the effect of the pressure difference between small and large particles, then the analogue is very close. The friction between the left-hand piston and the cylinder corresponds to the dissipation of chemical driving force by the interface reaction, which does not drive the process. Only  $P_1 - P_2$  does.