Exercises on Ch.6 Stability

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6.4 Summary of stability conditions

Exercise 6.4.1

The slope of the *G* versus *T* curve for a given substance at constant *P* is obtained as $(\partial G/\partial T)_P = -S$. If *S* is always positive, then this slope must always be negative. Examine if there is a similar rule for the curvature, $(\partial^2 G/\partial T^2)_P$.

Hint

Find a relevant stability condition, assuming that the system is stable.

Solution

 $(\partial^2 G/\partial T^2)_P = -(\partial S/\partial T)_P$ and in the ordinary energy scheme the conjugate pairs are (T,S), (-P,V) and (μ_i,N_i) . One of the stability conditions is thus $(\partial T/\partial S)_{P,Ni} > 0$. We can apply this because N_i is constant for a given substance. Thus, $(\partial^2 G/\partial T^2)_P = -(\partial S/\partial T)_P = -1/(\partial T/\partial S)_P < 0$. It should be noted that this result is quite general whereas the sign of S in $(\partial G/\partial T)_P = -S$ depends upon the choice of zero point for S.

Exercise 6.4.2

Formulate as many stability conditions as possible governing the change of U.

Hint

Consult Table 3.1 in Section 3.5. The important point is to define what variables should be kept constant.

Solution

The first set from the entropy scheme yields a number of conditions $\partial (-1/T)/\partial U > 0$ which can be written as $\partial T/\partial U > 0$ since $d(-1/T) = (1/T^2)dT$ and T > 0. Thus, $(\partial T/\partial U)_{P/T,\mu i/T} > 0$; $(\partial T/\partial U)_{v,\mu i/T} > 0$; $(\partial T/\partial U)_{P/T,Ni} > 0$; $(\partial T/\partial U)_{v,Ni} > 0$. The first set from the volume scheme yields $(\partial P/\partial U)_{T/P,\mu i/P} > 0$; $(\partial P/\partial U)_{S,\mu i/P} > 0$; $(\partial P/\partial U)_{T/P,Ni} > 0$; $(\partial P/\partial U)_{S,Ni} > 0$. In addition, one can let some μ_i/T and some N_i stay constant.

6.5 Limit of stability

Exercise 6.5.1

We have seen that $1/C_v > 0$ is a stability condition. Another one is $1/K_T > 0$ because $K_T = -1/V(\partial P/\partial V)_T$ and we know that $F_{vv} \equiv (\partial [-P]/\partial V)_T > 0$ is a stability condition. Show which one of the above conditions is more restrictive. Consider a substance with fixed composition.

Hint

Remember $C_v = T/(\partial T/\partial S)_v = T/U_{ss}$. In order to compare the values of $(\partial [-P]/\partial V)_T$ and $(\partial T/\partial S)_v$ the variables of one must be changed to those of the other. Change $(\partial [-P]/\partial V)_T$ to S and V using Jacobians.

Solution

The result will be $(\partial [-P]/\partial V)_T = U_{vv} - [(U_{sv})^2/U_{ss}]$ but $(\partial T/\partial S)_v = U_{ss}$. In a stable region $U_{vv} > 0$ and $U_{ss} > 0$ and now we see that it is necessary to have $U_{vv} > (U_{sv})^2/U_{ss}$ in order to satisfy the condition $(\partial [-P]/\partial V)_T > 0$. When coming closer to the stability limit, U_{ss} will decrease but, before it reaches zero, it will come to a value $U_{vv} = (U_{sv})^2/U_{ss}$ where $(\partial [-P]/\partial V)_T = 0$. We conclude that $1/K_T > 0$ is more restrictive than $1/C_v > 0$.

Exercise 6.5.2

We have found that the limit of stability of a unary system can be written as $F_{vv} = (\partial [-P]/\partial V)_{T,N} = 0$. Try to express this criterion in terms of derivatives of *G*.

Hint

Change variables from V and T to P and T by inverting the derivative.

Solution

 $F_{vv} = -(\partial P/\partial V)_{T} = -1/(\partial V/\partial P)_{T} = -1/G_{PP} = 0$ because $G_{P} \equiv (\partial G/\partial P)_{v} = V$. This gives $G_{PP} = -\infty$.

Exercise 6.5.3

Suppose that for some reason one would like to evaluate the limit of stability for a pure substance by studying the variation of *H*. Exactly what derivative should one use?

Hint

Using Table 3.1 in Section 3.5, find a form of the combined law having H as one of the variables and only one more extensive variable.

Solution

Line 5 in Table 3.1 is the only one listing *H*. We may take $N (= N_i \text{ for a pure substance})$ as the other extensive variable and should introduce (-P) instead of *V*/*T*. Then,

 $-d[(TS + PV)/T] - d[(-P)(V/T)] = -dS = (-1/T)dH - (V/T)d(-P) + (\mu/T)dN, \text{ and thus}$ $1/T = (\partial S/\partial H)_{P,N}. \text{ The criterion for the stability limit is } S_{HH} = (\partial [1/T]/\partial H)_{P,N} = 0, \text{ i.e.}$ $(\partial T/\partial H)_{P,N} = 0.$

Exercise 6.5.4

We have seen that the most severe stability conditions are those with only one extensive variable among those kept constant, the one that defines the size, usually N for a pure substance, and all those conditions are equivalent. Try to define the same stability condition using only extensive variables.

Hint

Change variables using Jacobians.

Solution

One may, for instance, start from $(\partial T/\partial S)_P > 0$ and change variables to *S* and *V*. Exercise 5.5.2 shows that the result is $(\partial T/\partial S)_P = U_{ss} - (U_{sv})^2/U_{vv}$. The stability condition may thus be written

$$\begin{vmatrix} U_{SS} & U_{VS} \\ U_{SV} & U_{VV} \end{vmatrix} > 0$$

This matrix has actually been called stiffness matrix.

6.6 Limit of stability of alloys

Exercise 6.6.1

Darken and Gurry (1953) defined an excess stability for binary solutions, $\alpha = {}^{E}G_{2}/x_{1}^{2}$. Darken (1967) instead proposed $\alpha = g_{22} - RT/x_{1}x_{2}$. Show how this second α is related to the excess Gibbs energy.

Hint

Start from $G_{\rm m} = x_1^{\rm o}G_1 + x_2^{\rm o}G_2 + RT(x_1\ln x_1 + x_2\ln x_2) + {}^{\rm E}G_{\rm m}$.

Solution

$$g_{2} = -{}^{o}G_{1} + {}^{o}G_{2} + RT(-1 - \ln x_{1} + 1 + \ln x_{2}) + d^{E}G_{m} / dx_{2};$$

$$g_{22} = RT(1/x_{1} + 1/x_{2}) + d^{2E}G_{m} / dx_{2}^{2};$$

$$\alpha = [RT(x_{2} + x_{1})/x_{1}x_{2} + d^{2E}G_{m} / dx_{2}^{2} - RT/x_{1}x_{2} = d^{2E}G_{m} / dx_{2}^{2}]$$

6.8 Limit of stability in phases with sublattices

Exercise 6.8.1

A simple model of a ternary solution gives the following expression: $G_{\rm m} = x_{\rm A}^{\circ}G_{\rm A} + x_{\rm B}^{\circ}G_{\rm B}$ + $x_{\rm C}^{\circ}G_{\rm C} + RT(x_{\rm A}\ln x_{\rm A} + x_{\rm B}\ln x_{\rm B} + x_{\rm C}\ln x_{\rm C}) + x_{\rm A}x_{\rm B}L_{\rm AB} + x_{\rm B}x_{\rm C}L_{\rm BC} + x_{\rm A}x_{\rm C}L_{\rm AC}$, where $L_{\rm AB}$, $L_{\rm BC}$ and $L_{\rm AC}$ are regular solution parameters for the three binary systems.

Positive *L* values result in miscibility gaps on the binary sides which extend into the ternary system. When a homogeneous alloy is cooled inside a miscibility gap it can remain metastable but below a sufficiently low temperature it becomes unstable. Derive an equation for the calculation of that temperature limit for a given alloy composition.

Hint

For the composition there are two independent variables, e.g. x_B and x_C , and x_A must then be regarded as $1 - x_B - x_C$.

Solution

Let x_{B} be variable 1 and x_{C} be variable 2. We find $g_{1} = -\circ G_{A} + \circ G_{B} + RT(-\ln x_{A} + \ln x_{B}) + (-x_{B} + x_{A})L_{AB} + x_{C}L_{BC} - x_{C}L_{AC}; g_{2} = -\circ G_{A} + \circ G_{C} + RT(-\ln x_{A} + \ln x_{C}) - x_{B}L_{AB} + x_{B}L_{BC} + (-x_{C} + x_{A})L_{AC}; g_{11} = RT(1/x_{A} + 1/x_{B}) + (-1 - 1)L_{AB}; g_{12} = RT(1/x_{A}) - L_{AB} + L_{BC} - L_{AC} = g_{21}; g_{22} = RT(1/x_{A} + 1/x_{C}) + (-1 - 1)L_{AC}.$ The criterion for limit of stability gives $g_{11}g_{22} = g_{12}g_{21}$. $(RT)^{2}(1/x_{A}^{2} + 1/x_{A}x_{B} + 1/x_{A}x_{C} + 1/x_{B}x_{C}) - 2L_{AC}RT(1/x_{A} + 1/x_{B})$ $-2L_{AB}RT(1/x_{A} + 1/x_{C}) + 4L_{AB}L_{AC} = (RT)^{2}/x_{A}^{2} + 2(-L_{AB} + L_{BC} - L_{AC})RT/x_{A} + L_{AB}^{2} + L_{BC}^{2}$ $+ L_{AC}^{2} - 2L_{AB}L_{BC} - 2L_{BC}L_{AC} + 2L_{AB}L_{AC}; (RT)^{2}(1/x_{A}x_{B} + 1/x_{A}x_{C} + 1/x_{B}x_{C}) - 2L_{AC}RT/x_{B}$

It is reassuring to see that this equation is symmetric with respect to all three components.

It does not matter which x was chosen to be the dependent variable. The numerical value of the temperature limit can easily be evaluated by inserting the alloy composition.

6.9 Le Chatelier's principle

Exercise 6.9.1

In Exercise 6.9 we considered a container of constant volume and with water and water vapour. The question was what would happen after adding some amount of heat. The vapor would try to expand and thus raise the pressure as an immediate result of heating. That may cause some condensation and thus a further increase of the temperature due to the heat of condensation. On the other hand, the heating of the vapor would increase the vapor pressure and thus cause evaporisation and a temperature decrease unless the pressure from the expansion of the vapor has already increased the vapor pressure more than the equilibrium vapour pressure of water has increase due to the heating. It was argued that Le Chatelier's principle predicts that the heating of the water dominated and there will be some evaporisation and a temperature decrease. Now examine what one may thus conclude about the variation of the equilibrium vapor pressure with temperature.

Hint

Suppose the vapor can be approximated as an ideal gas, PV = RT, and the vapor pressure can be represented with $P = K \cdot \exp(-Q/RT)$.

Solution

The heating will change the pressure of the already existing vapor by dP/dT = R/V but the equilibrium vapor pressure by $dP/dT = P \cdot (+Q/RT^2)$. The principle requires that $PQ/RT^2 > R/V$. Inserting PV = RT we find Q > RT. This should hold for all condensed substances.

Exercise 6.9.2

Test Le Chatelier's principle on the change of pressure during a similar experiment where the volume is increased isothermally and then kept constant for a long time.

Hint

At equilibrium at a given temperature water has a certain vapour pressure, the equilibrium pressure.

Solution

The volume increase will result in an instantaneous decrease of the pressure. The equilibrium is thus disturbed and during a second stage there will be further evaporation and the pressure will increase in agreement with Le Chatelier's principle. If the second stage also occurs under isothermal conditions, the pressure will return to its initial value. Evidently, this is a case where $(\partial Y^{b}/\partial X^{b})_{D=0} = 0$.

Exercise 6.9.3

Test Le Chatelier's principle on the change of volume during a similar experiment where the pressure is decreased isothermally and then kept constant for a long time.

Solution

The pressure decrease will result in an initial increase of the volume. Then there will be a further increase during a second stage due to further evaporation. This is in apparent contradiction to Le Chatelier's principle but in full agreement with the inverse form of the principle. It may be interesting to note that, if the external temperature and pressure are kept constant in this experiment, the process will not stop until all the water has evaporated.

Exercise 6.9.4

Somebody has objected to Le Chatelier's principle by referring to the following case. Consider a two-phase system of liquid water–water vapour at constant temperature. It is an experimental fact that an increase in pressure will give an immediate compression and then there will be a further compression due to an internal process, – spontaneous condensation at the increased pressure. Thus, the change due to the internal process will go in the same direction as the primary change, but would not Le Chatelier's principle require it to go in the opposite direction?

Hint

Identify what is a potential and what is an extensive variable.

Solution

The experimental fact concerns the change of volume, which is an extensive quantity, caused by a change of pressure, which is its conjugate potential. Le Chatelier considered the change of a potential, caused by a change of an extensive quantity. Thus we should expect the opposite result.