

ÉCOLE POLYTECHNIQUE DE MONTRÉAL

Département de génie chimique

Programme de matériaux

MET6208

ÉNERGÉTIQUE DES SOLUTIONS

SOLUTIONNAIRE

CONTRÔLE II

Mercredi le 26 mars 2014

14h00-17h30

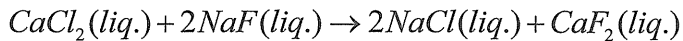
NOTES :

- Open book exam
- There are 6 questions and 2 figures

Professeur : Arthur D. Pelton

**Question 1 (3 points)**

For the exchange reaction :

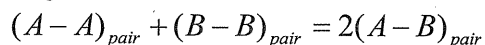


$\Delta G^{\text{exchange}}$  is very negative.

Sketch the expected form of the phase diagram (T versus composition) of the pseudobinary system  $\text{CaF}_2$  -  $\text{NaCl}$ . There is no solubility in the solid phases and there are no solid intermediate compounds. The melting point of  $\text{CaF}_2$  is higher than that of  $\text{NaCl}$ .

**Question 2 (3 points)**

- a) Using the quasichemical model, write an expression for the configurational entropy of mixing  $\Delta S^{\text{config}}$  of one mole ( $n_A + n_B = 1.0$ ) of a binary solution A-B of components A and B as a function of the component mole fractions  $X_A$  and  $X_B$ , the bond fractions  $X_{AA}$ ,  $X_{BB}$  and  $X_{AB}$ , the coordination number  $Z$  (assume  $Z_A = Z_B = Z = \text{constant}$ ) and the energy change  $\omega$  of the pair exchange reaction :



- b) Calculate  $\Delta S^{\text{config}}$  at  $X_A = X_B = 0.5$  when :

- i)  $Z=2, \omega=0$
- ii)  $Z=6, \omega=0$
- iii)  $Z=2, \omega=-\infty$
- iv)  $Z=6, \omega=-\infty$

**Question 3 (3 points)**

Liquid alloys B-C of components B and C at 1000 K are regular solutions with  $g_{BC}^E = \omega X_B X_C$ .

Dilute solutions of component A in pure liquid B at 1000 K are Henrian, with constant activity coefficient  $\gamma_{A(B)}^\circ$ .

Dilute solutions of component A in pure liquid C at 1000 K are Henrian, with constant activity coefficient  $\gamma_{A(C)}^\circ$ .

Write an equation for the activity coefficient of A in dilute solutions of A in binary B-C alloys at 1000 K as a function of the mole fraction ratio  $X_C / (X_B + X_C)$ .

**Question 4 (4 points)**

The phase diagram of the system NaCl-CaCl<sub>2</sub> is given in Figure 1. All solid phase are stoichiometric. Assume that the liquid phase is sub-regular :

$$\Delta h = X_{NaCl} X_{CaCl_2} (a + bX_{CaCl_2})$$

$$s^E = 0$$

The enthalpies of fusion (assumed independant of T) are :

$$\Delta h_{fusion(NaCl)}^\circ = 28\,000 \text{ J/mol}$$

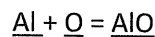
$$\Delta h_{fusion(CaCl_2)}^\circ = 28\,400 \text{ J/mol}$$

- i) Calculate the sub-regular solution parameters « a » and « b ».
- ii) Calculate the enthalpy and entropy of fusion of the compound 4NaCl • CaCl<sub>2</sub>.

**Question 5 (3 points)**

Aluminium is added to liquid Fe as a deoxidizer to remove dissolved oxygen by precipitating it as solid Al<sub>2</sub>O<sub>3</sub>. Initially, as Al is added, the dissolved oxygen content decreases as expected, but beyond a certain « deoxidation minimum », the oxygen content begins to increase again as additional Al is added. (See Figure 2.)

Show that this behaviour is predicted by a model in which dissolved Al and O atoms combine to form dissolved AIO molecules in an ideal Henrian solution (with Al, O, and AIO all mixing ideally on a single lattice) when the equilibrium constant of the reaction



is very large. (That is, the driving force to form the AIO molecules is very large). (The axes of Figure 2 are total dissolved oxygen (as O plus AIO) and total dissolved aluminum (as Al plus AIO)).

NOTE : You do not have to derive an equation for the deoxidation minimum. You need only explain in words why there is a deoxidation minimum.

**Question 6 (4 points)**

The system is an ordered solid alloy  $AB_{(2\pm\delta)}$ . When the compound is completely ordered (at 0K), A atoms occupy only the « A-sublattice » and B atoms occupy only the « B-sublattice ».

At higher temperatures, the majority defects are vacancies on the A-sublattice and vacancies on the B-sublattice.

Using the Compound Energy Formalism, write an expression for the Gibbs energy of the solution, per mole of lattice sites, as a function of the site fractions and of the end-member Gibbs energies. (You may ignore the second-nearest-neighbour interaction terms ( $g^E$ ) and the short-range-order term. Consider only the terms containing the end-member Gibbs energies and the configurational entropy terms.)

The end-member Gibbs energies are the « formalism parameters ». What are the « model parameters »? Express the formalism parameters in terms of the model parameters.

Show how the model parameters affect the width of the single-phase region of homogeneity of  $AB_{(2\pm\delta)}$  in the A-B phase diagram.

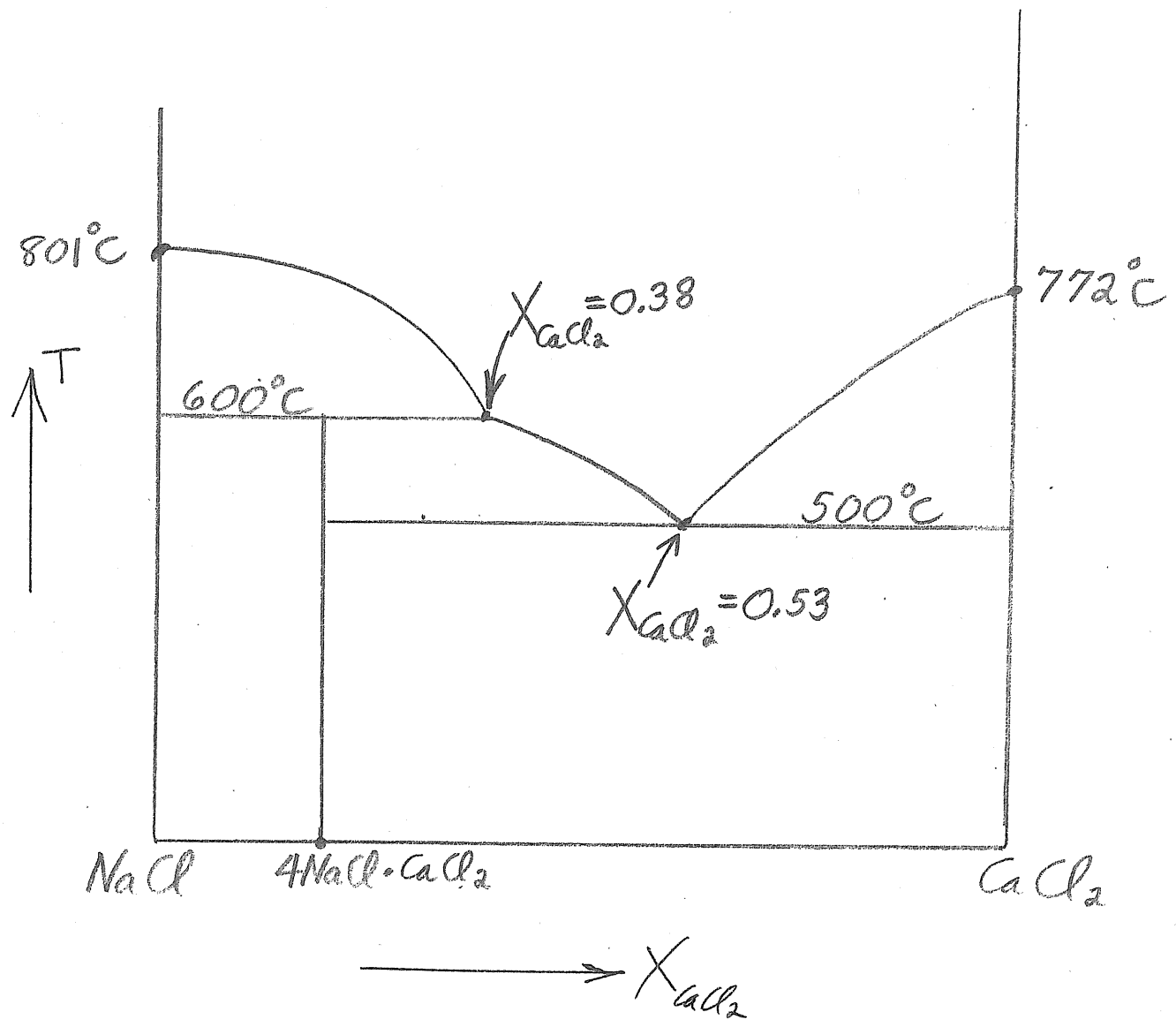


Figure 1

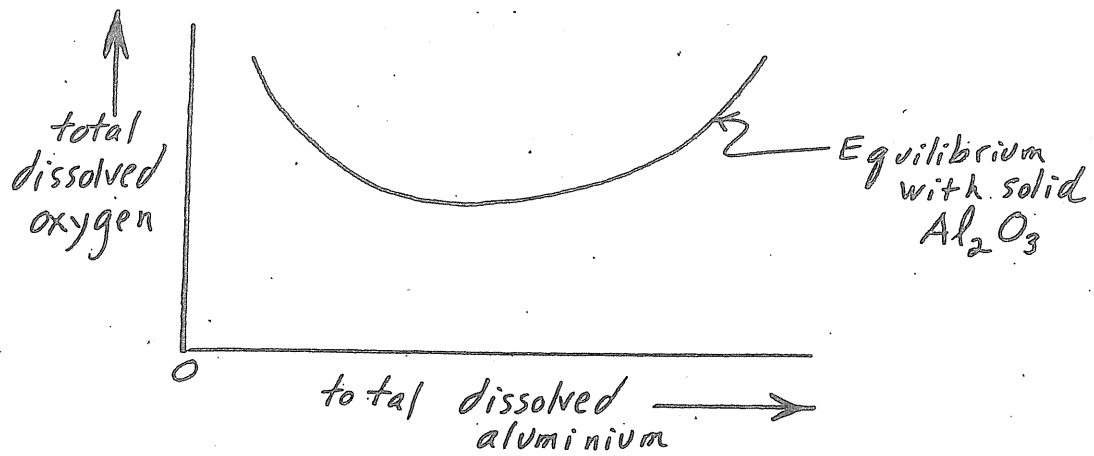
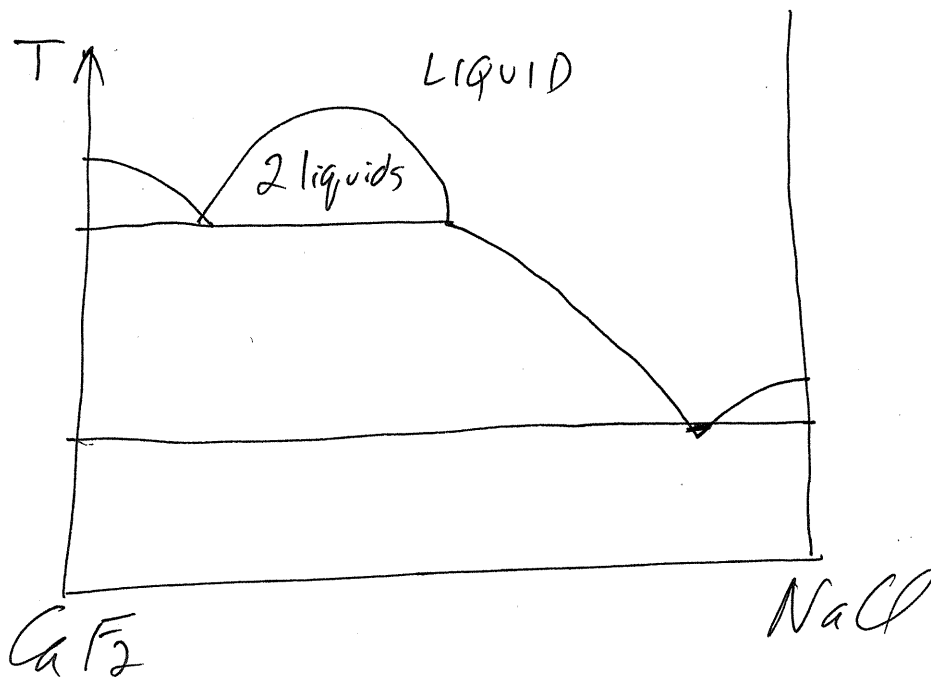


Figure 2

## Question 1

Strong positive deviations along main diagonal, yielding a miscibility gap.



$$\rightarrow (a) \Delta S^{\text{config}} = -R(X_A \ln X_A + X_B \ln X_B)$$

Question 2

$$-\frac{RZ}{2} \left( X_{AA} \ln \frac{X_{AA}}{X_A^2} + X_{BB} \ln \frac{X_{BB}}{X_B^2} + X_{AB} \ln \frac{X_{AB}}{2X_A X_B} \right)$$

(b) (i) When  $w=0$  the solution is ideal;  $X_{AA}=X_A^2$ , etc  
and  $\Delta S^{\text{conf.}} = -R(X_A \ln X_A + X_B \ln X_B)$  So:  $\Delta S = 5.764 \text{ J/mol}$   
when  $X_A = X_B = 0.5$

(ii) Same as (i)  $\Delta S = 5.764 \text{ J/mol}$ .

(iii) When  $w = -\infty$ , when  $X_A = X_B = 0.5$ , the solution is fully ordered with only AB pairs. That is,  $X_{AA} = X_{BB} = 0$  and  $X_{AB} = 1$ .

When  $Z=2$ :

$$\begin{aligned} \Delta S &= -R(0.5 \ln 0.5 + 0.5 \ln 0.5) \\ &\quad - R\left(\frac{2}{2}\right) \left( 0 + 0 + \ln \frac{1}{2\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)} \right) \\ &= -R \ln(0.5) - R \ln(2) \\ &= \underline{\underline{0}} \end{aligned}$$

(iv) When  $Z=6$ :

$$\begin{aligned} \Delta S &= -R(0.5 \ln 0.5 + 0.5 \ln 0.5) \\ &\quad - R\left(\frac{6}{2}\right) \left( 0 + 0 + \ln \frac{1}{2\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)} \right) \\ &= -R \ln 0.5 - 3R \ln 2 \\ &= -2R \ln 2 \\ &= \underline{\underline{-11.527 \text{ J/mol}}} \end{aligned}$$



### Question 3.

$g_A^E = RT \ln \gamma_A$  will vary linearly with  $X_C / (X_B + X_C)$  from its value in the A-B binary to its value in the A-C binary.

As well, there will be a contribution from the excess Gibbs energy term in the B-C binary:  $g_{BC}^E = \omega X_B X_C$

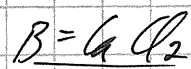
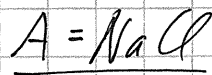
This term gives rise to a contribution to  $g_A^E$  of:

$$g_A^E = \frac{2}{2M_A} \left( \frac{(M_A + M_B + M_C) M_B M_C}{(M_A + M_B + M_C)^2} \right) \omega$$

$$= \frac{-\omega M_B M_C}{(M_A + M_B + M_C)^2} = -\omega X_B X_C$$

Hence:  $g_A^E = RT \left( \frac{X_B}{X_B + X_C} \ln \gamma_{A(B)}^0 + \frac{X_C}{X_B + X_C} \ln \gamma_{A(C)}^0 \right) - \omega X_B X_C$

$$\ln \gamma_A = \left( \frac{X_B}{X_B + X_C} \ln \gamma_{A(B)}^0 + \frac{X_C}{X_B + X_C} \ln \gamma_{A(C)}^0 \right) - \frac{\omega X_B X_C}{RT}$$

Question 4

(i)  $\Delta h = X_A X_B (a + b X_B)$

$$\Delta h_A = \frac{d(\Delta H)}{dX_A} = \frac{2}{2X_A} \frac{(M_A \cdot M_B)}{(M_A + M_B)} \cdot (M_A + M_B) \left( a + b \frac{M_B}{M_A + M_B} \right)$$

$$= X_B^2 \left[ (a-b) + 2b X_B \right] = \Delta g_A$$

$$\Delta h_B = X_A^2 (a + 2b X_B) = \Delta g_B$$

On NaCl liquidus:  $RT \ln X_A + \Delta g_A = -\Delta h_{fus(A)}^\circ \left( 1 - T/T_{fus(A)}^\circ \right)$

Point on liquidus at  $X_B = 0.38$  at  $873\text{ K}$ 

$$R(873) \ln(0.62) + (0.38)^2 (a - b + 2(0.38)b) = -28000 \left( 1 - \frac{873}{1073} \right)$$

$$a - 0.24b = -12305$$

On CaCl<sub>2</sub> liquidus:  $RT \ln X_B + \Delta g_B = -\Delta h_{fus(B)}^\circ \left( 1 - T/T_{fus(B)}^\circ \right)$

Point on liquidus at  $X_B = 0.53$  at  $773\text{ K}$ 

$$R(773) \ln(0.53) + (0.47)^2 (a + 2b(0.53)) = -28400 \left( 1 - 773/1073 \right)$$

$$a + 1.06b = -14955$$

Solve:  $a = -12795$        $b = -2038$

(ii) On liquidus of A<sub>4</sub>B:  $RT \ln a_{A_4B} = -\Delta h_{fus}^\circ + T \Delta S_{fus}^\circ$

$$RT \ln \frac{X_A^4 X_B}{(0.8)^4 (0.2)} + 4\Delta h_A + \Delta h_B - 4\Delta h_A \Big|_{(X_A=0.8)} - \Delta h_B \Big|_{(X_B=0.2)}$$

$$= -\Delta h_{fus}^\circ + T \Delta S_{fus}^\circ$$

$$RT \ln \left( \frac{X_A^4 X_B}{0.0819} \right) + 4X_B^2 (-10760 - 4075 X_B) + X_A^2 (-12795 - 4075 X_B)$$

$$-4(0.2)^2 (-10760 - 4075(0.2)) - (0.8)^2 (-12795 - 4075(0.2)) = -\Delta h_{fus}^\circ + T \Delta S_{fus}^\circ$$

(Question 4 continued)

$$RT \ln \left( \frac{X_A X_B}{0.0819} \right) + 4X_B^2(-10760 - 4075X_B) \\ + X_A^2(-12795 - 4075X_B) + 10560 \\ = -\Delta H_{\text{fusion}}^{\circ} + T\Delta S_{\text{fusion}}^{\circ}$$

Point on liquidus at 873 K,  $X_B = 0.38$  gives:

$$-4800 = -\Delta h_{\text{fusion}}^{\circ} + 873 \Delta S_{\text{fusion}}^{\circ}$$

Point on liquidus at 773 K,  $X_B = 0.53$  gives:

$$-19665 = -\Delta h_{\text{fusion}}^{\circ} + 773 \Delta S_{\text{fusion}}^{\circ}$$

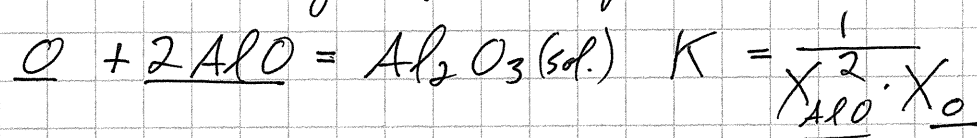
Solving:  $\Delta h_{\text{fusion}}^{\circ} = 90920 \text{ J/mol A}_x\text{B}$

$$\Delta S_{\text{fusion}}^{\circ} = 98.66 \text{ J/mol A}_x\text{B}$$

$$\text{(Congruent fusion } T = \left( \frac{90920}{98.66} - 273 \right) = \underline{649^{\circ}\text{C}})$$

Question 5      Al + O  $\rightleftharpoons$  AlO

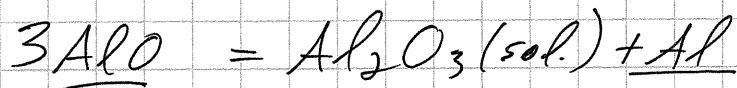
- At low Al and high O, main species are O and Al



$$X_{\text{total Al}} \approx \underline{X_{AlO}} \quad X_{\text{total O}} \approx \underline{X_O}$$

Hence as Al content increases, O content decreases

- At high Al and low O, main species are AlO and Al



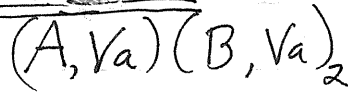
$$X_{\text{total O}} \approx \underline{X_{AlO}}$$

$$X_{\text{total Al}} \approx \underline{X_{Al}}$$

$$K = \frac{\underline{X_{Al}} (10)}{\underline{X_{AlO}}^3}$$

So as Al content increases,  
O content increases.

Question 6:



$\begin{cases} y_i' = \text{site fractions on A-sublattice} \\ y_i'' = \text{site fractions on B-sublattice} \end{cases}$

$$g = y_A' y_B'' g_{AB_2}^0 + y_A' y_{Va}'' g_{AVa_2}^0 + y_{Va}' y_B'' g_{VaB_2}^0 + y_{Va}' y_{Va}'' g_{VaVa_2}^0 + RT(y_A' \ln y_A' + y_{Va}' \ln y_{Va}') + 2RT(y_B'' \ln y_B'' + y_{Va}'' \ln y_{Va}'')$$

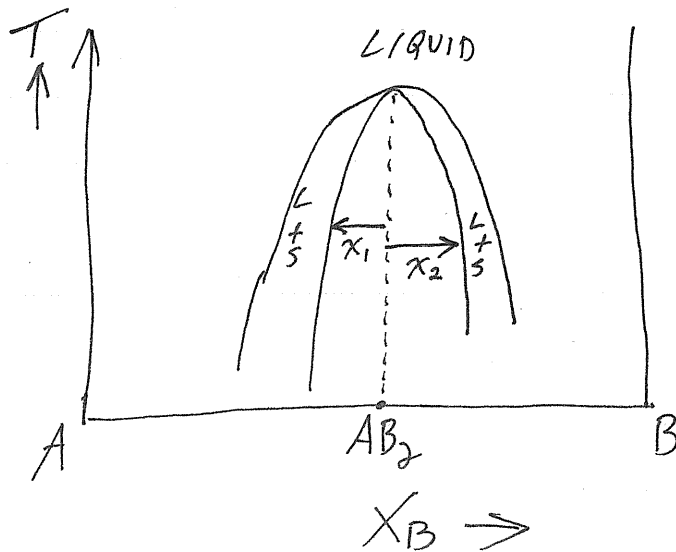
where:  $\begin{cases} y_A' + y_{Va}' = 1 \\ y_B'' + y_{Va}'' = 1 \end{cases}$

Model parameters:

- (1)  $g_{AB_2}^0 =$  Gibbs energy of vacancy-free  $AB_2$  stoichiometric
- (2)  $(g_{VaB_2}^0 - g_{AB_2}^0) = \Delta g_1 =$  Gibbs energy to form  $\frac{1}{2}$  mol of vacancies on the A-sublattice
- (3)  $(g_{AVa_2}^0 - g_{AB_2}^0) = \Delta g_2 =$  Gibbs energy to form 2 mol of vacancies on the B-sublattice

Note also:  $(g_{VaVa_2}^0 - g_{AB_2}^0) = \Delta g_3 =$  Gibbs energy to form vacancies on both sublattices.

That is:  $\Delta g_3 = \Delta g_1 + \Delta g_2$



As  $\Delta g_1$  increases, the distance  $x_2$  increases, and as  $\Delta g_2$  increases, the distance  $x_1$  increases.