Parameter assessment of Fe-Cr system at equilibrium state by ThermoCalc

CME 572 Advanced Thermodynamic

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Lu Yingjie

Define the binary system



Calculation of the phase diagram

(a) After defining the system as Fe-Cr binary system, start up the T-X calculation by creating new successor for equilibrium calculation. Based on the Gibbs phase rule for 2D plots, F=C-P+1, C=2 for a binary system, the maximum degree of freedom is 2 in single phase region. Thus, only two condition variables can be defined. In this case, the variables are set as temperature and mass percent of Cr, the pressure is consistent as 1 atmospheric. System size is set as 1 mole for easy calculation. X-axis is defined as mass percent of Cr, range from 0 to 100 linearly. Y-axis is defined as Kelvin's temperature, range form room temperature, i.e., 298K to 3000K linearly. The setup is shown in the snapshot below.

Project 🗗 🕂 🛪	Configuration			
		Т	-X calculations	
	Conditions Functions Options			
My Project	Number of missing conditions is 0			
Sustan Dation 1	Condition Definitions			
G-X separate phases	💿 💿 🗹 Temperature	∽ Kelvin	√ 1000.0	
	💿 🥥 📝 Pressure	 ✓ Atmospheres 	✓ 1.0	
T-X calculations G-X calculations	🗿 🤤 🗹 System size	∼ Mole	✓ 1.0	
-	🗿 😑 🗌 Mass percent Fe	∼] [Fe	\sim] [Mass percent \sim	99.99
hase diagram	💿 🤤 🗹 Mass percent Cr	~] [Cr	\sim Mass percent \sim	0.01
Activity	Calculation Type			
G-X all phase	○ Single equilibrium ○ One axis	⊖ Grid	hase diagram	
	Axis Definitions			
	Quantity Min	Max	Step division Ty	pe
Scheduler 🗗 무 兴	💿 🤤 🗹 Mass percent Cr 🗸 0.0	100.0	50.0 L	inear - min no. of steps \sim
🔅 Scheduled Jobs	③	3000.0	50.0 L	inear - min no. of steps \sim

Next start up a plot renderer to define the parameters for phase diagram. The magnitude of tielines' density is the highest. To show the stable phase only. No information about sublattice or axis quantity will be displayed in the phase diagram. The definition of x-axis and y-axis remain unchanged, except the temperature top limit is reduced to 2500K. The setup is shown in the snapshot below.

Project	⊡ ₽ ×	Configuration			
		🖄 phase diagram			
My Project System Definer 1 G-X separate phases T-X calculations G-X calculations	-X separate phases	Image: Show Triangular Image: Show Grid Image: Show Grid	~		
	lculations	X-axis			
		Axis variable: Composition V Cr V Mass percent V	Mass percent \checkmark		
hase diagram		Axis type: Linear V			
Activity	4	Limits: 0.0 to 100.0 step 10.0 I Automatic scaling			
G-X all p	phase	Y-axis			
		Axis variable: Temperature			
		Axis type: Linear			
Scheduler	а т ×	Limits: 298 to 2500.0 step 220.0 Automatic scaling			
🔅 Scheduled Jobs					

(b) Phase diagram is shown below.



- (c) The highest melting point is 2179.99K when Cr is 100wt%. The lowest melting point is 1788.80K when Cr is 19.96wt%. For unary systems, melting point of pure Fe is 1810.86K when Cr is 0wt%, melting point of pure Cr is 2179.99K when Cr is 100wt%.
- (d) The intermediate phase in this system is the sigma phase.
- (e) At room temperature the stable phase for Fe is BCC_A2 phase, for Cr is BCC_A2#2 phase. These two phases have the same lattice structure but different compositions, also, they repel each other at this equilibrium state.

Calculation of Gibbs energy

(a) The condition definitions of the system remain the same. In this case, Gibbs free energy of one phase is a function of composition. Therefore, the calculation type is set as "one axis", and the variable is mass percent of Cr, range from 0 to 100 linearly.

Project 🗗	Ψ×	Configuration										
		Conditions	Function	s Options		🔳 G	X calc	ulations				
My Project		Number of missing conditions is 0 Switch to sin										
Sustam Definer 1		Condition Definitions										
G-X separate ph	ases	0 🛛 🗸	Tempera	ature	~	Kelvin	~	1000				
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T-X calculations G-X calculations		0 🤤 🗸	System s	size	~	Mole ~		1.0				
ase diagram Activity G-X all phase		🔘 🤤 🗌 Mass percent Fe			~	Fe	\sim	Mass percent V	99.99			
		0 🔾 🗸	Mass percent Cr 🗸 🗸		Cr ~		Mass percent V	0.01				
		Calculation Type Single ec	e uilibrium	One axis	⊖ Grid		Phase	diagram				
		Quantity		Min	Max	Step divis	ion	Туре		Step Method		
Scheduler 🗗	φ×	Mass percer	nt Cr 🗸 🗸	0.0	100.0	50.0		Linear - min no	o. of steps 🛛 🗸	Normal ~		
🔅 Scheduled Jobs												

To plot the all-phase G-X curves, the Y-axis variable is set as Gibbs energy per mole for all phases. Since the Gibbs energy data of each phase has been relative to the "standard element reference" (SER) in the CALPHAD database¹, the SER can remain uncheck. The legend can be set as "stable phases" or "axis quantity", the difference is that the former setting shows the Gibbs energy of the two-phase region, but the latter setting doesn't.

	🖄 G-X all phase
My Project	Save Diagram Show Triangular Show Grid Switch Axes Retain Labels Table View
System Definer 1	G-X calculations
	gend option: Axis quantity V Legend style: None V
T-X calculations G-X calculations	(-axis
ka l	Axis variable: Composition
hase diagram	Axis type: Linear
Activity	Limits: 0.0 to 100.0 step 10.0 Automatic scaling
G-X all phase	/-axis
	Axis variable: Gibbs energy V Per mole V SER All phases V Joule V
	Axis type: Linear
Scheduler	Limits: 0.0 to 1.0 step 0.1

To plot the separate phases G-X curves, the Y-axis variable is set as no normalized Gibbs energy for all phases. The Gibbs energy value of each stable phase same as the value in all-phase G-X curves because the system size is 1 mole. The Gibbs energy curves of unstable phase are plotted as straight lines with pseudo values.

						2	G-X sep	arate phase	es				
My Project	Save Diagram S	how Triangular	Show Grid Sw	itch Axes Ret	ain Labe	Is Table Vie	w						
T-X calculations G-X separate phases	egend option:	Axis quantity	✓ Legend	style: Non	9		~						
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nase diagram Activity	Axis type: Limits:	Linear 0.0	to 100.0	step	10.0	 Image: A start of the start of	Automati	c scaling					
G-X all phase	Y-axis												
	Axis variable:	Gibbs energy			~	No normali	ization	~	SER	All phases	~	Joule	~
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In (b)-(d) and (f), the plots above left are all-phase G-X curves, above right show an enlarged area of the curves. the plots below left are separate-phase G-X curves, below right show an enlarged area of the curves. In (e), the plots above are all-phase G-X curves denoted by two types of legends, the plots below are separate-phase G-X curves denoted by the two corresponding types of legends.

(b) G-X curves at the highest melting point (2179.9K)





(e) G-X curves at 298K





At 2179.9K, the lowest Gibbs energy curve is the curve of liquid phase. It has an intersection point with the curve of BCC_A2 when the composition of the system is 100wt%Cr.

At 1788.8K, the lowest curve is the curve of BCC_A2 phase. This curve has an intersection point with the liquid Gibbs energy curve when the composition is around 20wt%Cr.

At 498K, the lowest Gibbs energy curve is the curve of BCC_A2 phase when the composition is smaller than 1.75wt%Cr and is the curve of BCC_A2#2 phase when the composition is larger than 99.12wt%Cr. When the composition is in between of these two values, this region is the miscibility gap, the lowest curve is the common tangent line. At 298K, the lowest Gibbs energy curve is the common tangent line in the entire composition range of Cr.

At 1000K, intermediate phase sigma_D8B exist when the composition of the system is between 41.7-48.7wt%Cr. The lowest curve is the curve of BCC_A2 phase between 0-29.36wt%Cr, is the common tangent of BCC_A2 and sigma_D8B between 29.36-41.7wt%Cr, is the curve of sigma_D8B between 41.7-48.7wt%Cr, is the common tangent of sigma_D8B and BCC_A2 between 48.7-63.79wt%Cr, is the curve of BCC_A2 when the composition is larger than 63.79wt%Cr.

The corresponding phases to the lowest Gibbs energy curves are labeled in the figures for different temperatures.

In the miscibility gap, $\Delta G_{mix} = \Delta G_{mix}^{xs} + \Delta G_{mix}^{ideal} = a_0 X_1 X_2 + RT(X_1 \ln X_1 + X_2 \ln X_2)$ (1), using the regular solution model.

Calculations of activities

(a) Start up a new branched calculation by select the "plot renderer" using the same G-X setup parameters. This time set two Y-axes with activity of Cr and Fe refer to phase BCC_A2 separately, set X-axis as the mole fraction of Cr. When the two components are completely miscible in the phase, the a-X curve is a continuous curve with the slope of each point on the curve equal to the activity coefficient γ of the selected component.

System Definer 1	🔲 G-X calcula	tions								
G-X separate	Legend option:	Axis quantity	 Legend style: 	None		~	Flexible mode V			
T-X calculations G-X calculations	X-axis									
10	Axis variable:	Composition		~ (Cr v	Mole fraction				
nase diagram	Axis type:	Linear	~							
Activity	Limits:	0.0 t	o 1.0	step 0.1		Automatic scaling				
G-X all phase	Y-axis									
	Axis variable:	Activity referred	to a phase	~	BCC_A2	✓ Fe ✓				
	Axis type:	Linear	~							
Scheduler 급 무 ×	Limits:	0.0 t	o 1.0	step 0.1		Automatic scaling				
Scheduled Jobs										
	X-axis									
	Axis variable:	Composition		~ 1	Cr 🗸	Mole fraction				
	Axis type:	Linear	~							
	Limits:	0.0 t	o 1.0	step 0.1		Automatic scaling				
	Y-axis									
	Axis variable:	Activity referred	to a phase	~	BCC_A2	~ Cr ~				
	Axis type:	Linear	~							
	Limits:	0.0 t	o 1.0	step 0.1		Automatic scaling				

(b) a-X curves at 498K



When the composition of the system is smaller than 0.019mol%Cr (BCC_A2 phase) or greater than 0.99mol%Cr (BCC_A2#2 phase), the two components are completely miscible, both can be considered as dilute solutions. At BCC_A2 phase, Cr is the solute and Fe as the solvent. The slop of the segment of the red a-X curve in this composition region is greater than 1, means that the system exhibits a positive departure from the ideal solution at this phase. At BCC_A2#2 phase, Fe is the solute and Cr is the solvent. Based on the Henry's law: $\lim_{X_{Cr} \to 1} a_{Fe} = \gamma_{Fe}^0 (1 - X_{Cr}), \text{ the } \gamma_{Fe}^0$, i.e., the tangent of a_{Fe} -X_{Cr} curve when $X_{Fe} \to 0$ is significantly greater than 1. So, at this phase, the system exhibits a positive departure as well.

In the two-phases region, i.e., miscibility gap, use partial molal molar excess Gibbs free energy $\Delta \overline{G_{Cr}^{xs}}$ to determine the activity of a component. According to the formula $\Delta \overline{G_1} = \Delta G_{mix} + \frac{d\Delta G_{mix}}{dX_1}(1-X_1)$ (2) and the equation of ΔG_{mix} (1), $\Delta \overline{G_1} = \Delta \overline{G_{Cr}} = \Delta \mu_{Cr}$ can be calculated. Also, as $\Delta \mu_1 = \Delta \overline{G_1^{xs}} + \Delta \overline{G_1^{ideal}}$ (3) and $\Delta \overline{G_1^{ideal}} = RT \ln X_1$ (4), $\Delta \overline{G_{Cr}^{xs}}$ can be calculated by integrating (1)(2)(3)(4) four equations and the result is $\Delta \overline{G_{Cr}^{xs}} = a_0 X_2^2$. Hence, if a_0 is positive, this partial molal molar excess Gibbs free energy of Cr is positive, the relationship between these two components is repulsive and the system exhibits a positive departure from the ideal solution. Same process for Fe.

(c) a-X curves at the lowest melting point (1788.8K)



With respect to the guidelines, it's clear to see that at this temperature, the system exhibits positive departure from the ideal solution at the BCC_A2 phase.

References:

- 1. https://tsapps.nist.gov/publication/get_pdf.cfm?pub_id=918377
- 2. https://ntrs.nasa.gov/api/citations/19990116716/downloads/19990116716.pdf