

國立清華大學命題紙

98 學年度 工程與系統科學系甲組碩士班入學考試

科目 材料熱力學 科目代碼 2602 共 2 頁第 1 頁 *請在【答案卷卡】內作答

1. The Helmholtz free energy, F , is a function of volume (V) and temperature (T), giving the differential of dF , (1) write down the fundamental equation of dF in terms of dV and dT . (5%), and (2) write the differential dF explicitly in terms of variations in T and P , where P is pressure. The word "explicitly" means that do not leave any partial differentials in the expression for dF , but express everything in terms of measurable properties such as P , V , T , α , β , C_p , or C_v , or state functions such as U , H , S , where α is the thermal expansion coefficient, β is the compressibility, C_p and C_v are heat capacities at constant pressure and at constant volume respectively, U is the internal energy, H is the enthalpy and S is the entropy of the system. (15%)
2. Read *carefully* and first give the answer to the following statements, and then briefly indicate your thermodynamic reasoning and/or thermodynamic equations. You should give your reason in each question; otherwise, no credits will be given for the question.
- (A) A material (closed system) at constant pressure undergoes a reversible phase transition with temperature at $T = T_0$. Please give your answer whether the following statements are always true, true only part of the time, or never true.
- (1) At the phase transition temperature T_0 , the high temperature phase has a higher volume than the low-temperature phase:
_____ NEVER TRUE _____ ALWAYS TRUE _____ TRUE PART OF THE TIME (3%)
- (2) At the phase transition temperature T_0 , the high temperature phase has a higher entropy than the low-temperature phase:
_____ NEVER TRUE _____ ALWAYS TRUE _____ TRUE PART OF THE TIME (3%)
- (3) At the phase transition temperature T_0 , the high temperature phase has a higher enthalpy than the low-temperature phase:
_____ NEVER TRUE _____ ALWAYS TRUE _____ TRUE PART OF THE TIME (3%)
- (4) At the phase transition temperature T_0 , the high temperature phase has a higher Gibbs free energy than the low-temperature phase:
_____ NEVER TRUE _____ ALWAYS TRUE _____ TRUE PART OF THE TIME (3%)
- (B) For a system with only pdV work, in an environment under constant pressure and temperature, the condition that $\Delta S_{\text{universe}} > 0$ is equivalent to:
_____ $\Delta G > 0$ _____ $\Delta G < 0$ _____ $\Delta H < 0$ _____ $\Delta H > 0$
_____ $\Delta S < 0$ _____ $\Delta S > 0$
- In the above, the state functions (G, H, S) refer to properties of the system. (4%)
- (C) At constant composition, does the free energy increase or decrease with increasing temperature?
_____ INCREASE _____ DECREASE (4%)

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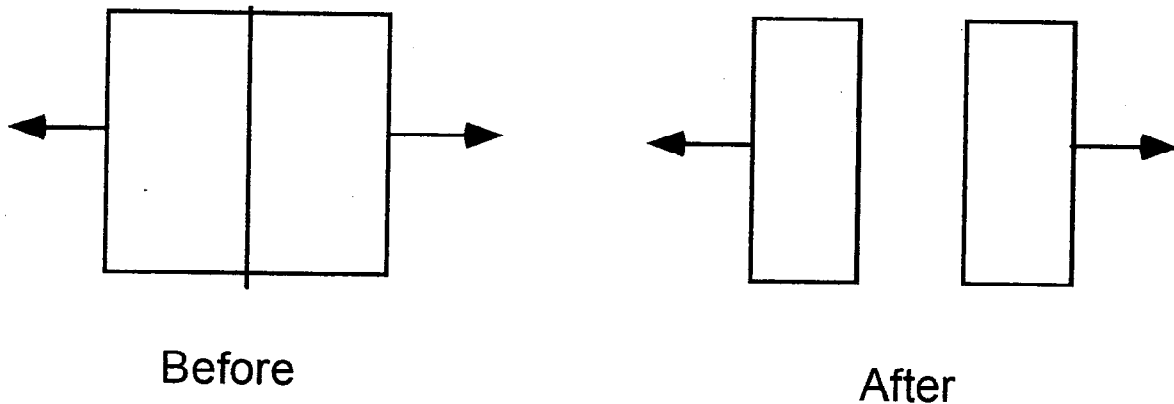
科目 材料熱力學 科目代碼 2602 共 2 頁第 2 頁 *請在【答案卷卡】內作答

3. The work performed in creating surfaces can be added to the work flows in the First Law of Thermodynamics. If σ is defined as the surface energy per unit area, the work performed when creating new surface is σdA , where A is the surface area of the system. Silicon (Si) has a surface energy (solid-gas) which over the temperature range of interest increases with temperature as $B + C \ln(T)$ with C and B positive constants. A single crystal of Si is reversibly pulled apart as show in the figure below. The crystal is insulated so that there is no heat flow to the environment.

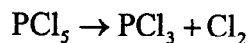
(1) Calculate the change in entropy of the system (per unit new surface area) as the crystal is isothermally and reversibly pulled apart. Answer can be in terms of constants B , C , and Temperature. (10%)

(2) What happens to the temperature of the system if the crystal is pulled apart adiabatically (but reversibly). (10%)

Assume that there is no plastic deformation in the system while it is being pulled apart.



4. The equilibrium constant $K_p = 1.78$ at $T = 525$ K for the reaction



The reaction proceeds at constant volume. Find the total pressure p_o of an initial equi-molar mixture PCl_5 and Cl_2 (a mixture where the numbers of molecules of PCl_5 and Cl_2 are the same), if the partial pressure of PCl_5 in equilibrium is $p_{\text{PCl}_5} = 0.89$ atm. (20%)

5. For a first-order phase transition $\Delta G = 0$, $\Delta T = 0$, show that during a first-order phase transition

$$\Delta U = \Delta H \left(1 - \frac{d \ln T}{d \ln P} \right). \quad (20\%)$$