

MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
**Thermodynamics of Materials**

3.00 Fall 2002

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Problem Set 6: Due Mon. Nov. 4, Before 5PM in in 13-5114

**Exercise 6.1**

Methane  $\text{CH}_4$  and carbon dioxide  $\text{CO}_2$  are mixed in equal molar proportions in a reservoir fixed at  $T = 1750\text{K}$  and 1 atmosphere pressure. Find the equilibrium concentrations of the gaseous components.

Assume that the only gaseous components are  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$ .

Free energies as a function of temperature for several reactions are tabulated below:

Reaction	Change in Molar Gibbs Free Energy (joules)
$\text{CH}_4(\text{gas}) \rightleftharpoons \text{C}(\text{graphite}) + 2\text{H}_2(\text{gas})$	$69120 - 22.25T \log T + 65.35T$
$2\text{CO}(\text{gas}) \rightleftharpoons 2\text{C}(\text{graphite}) + \text{O}_2(\text{gas})$	$223400 + 175.3T$
$\text{CO}_2(\text{gas}) \rightleftharpoons \text{C}(\text{graphite}) + \text{O}_2(\text{gas})$	$394100 + 0.8T$
$\text{H}_2(\text{gas}) + \frac{1}{2}\text{O}_2(\text{gas}) \rightleftharpoons \text{H}_2\text{O}(\text{gas})$	$-246400 + 54.8T$

**Exercise 6.2**

Find an expression that relates the change in Gibbs free energy with temperature at constant volume,  $\left(\frac{\partial G}{\partial T}\right)_V$ , in terms of the, entropy, volume, thermal expansivity  $\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$ , and the isothermal compressibility  $\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$ .

Describe how you would measure  $\kappa_T$  and  $\alpha$  in an experiment.