Problem 1 (20 Points)

Consider the oxidation reaction of methane, which is carried out at constant pressure:

$CH_4 + \frac{1}{2} O_2 \rightarrow CH_3OH$

For this reaction $\Delta H = -164$ kJ/mol and $\Delta S = -162$ J/mol-K. Initially, there is 1 mole of CH_4 and 1 mole of ($\frac{1}{2} O_2$).

a) (8 Points) For what temperatures does this reaction proceed spontaneously?

Spontaneous : $\Delta G < 0$

$$\Delta G = \underset{\overset{\uparrow}{-}}{\Delta H} - \underbrace{T\Delta S}_{+}$$

So have $|\Delta H| = T_{crit} |\Delta S|$

$$T_{crit} = \frac{164{,}000 \text{ J/mol}}{162 \text{ J/mol}\cdot\text{K}}$$

$$= 1012 K$$

require $T < T_{crit}$

(b) (5 Points) If the reaction is carried out at 300 K, what happens to the entropy of the environment S_{env} ? (circle one)

$\Delta S_{system} = -162$ J/mol K (system S decreases)

$\Delta S_{env} = -\Delta S_{system} = +162$ J/mol K

[✓ increase] decrease stay the same

Problem 2 (30 Points)

A reversible heat engine is made of a very large block of ice at 273 K (0 °C) and 1 kg of water at 373 K (100 °C). The heat engine absorbs heat from the water and expels it to the ice until work can no longer be provided by the engine. The heat capacity of liquid water is 4.2 J/gK, and the heat of melting for ice is 333 J/g.

(a)(6 Points) At the completion of the process, what is the temperature of the water?

As heat is extracted from water, its temperature drops. $T_H - T_c$ is reduced so efficiency drops. Cycle ends when water + ice are at same T

For "very large block of ice" $T_{ice} = T_c = 0°C$ always

$T_{water} = 0°C \ (273K)$

(Explanation was not required)

(b) (9 Points) At the completion of the process, what is the total amount of heat Q_H that was extracted from the water?

$$Q_H = m\, C_v^{H_2O} \Delta T$$

$$= (1\,kg)(4200 \frac{J}{kg\,K})(100K) = 4.2 \times 10^5\, J$$

c) (8 Points) What is the efficiency ε of the heat engine when the water has been cooled to 300 K?

$$\varepsilon(T) = \frac{T - T_c}{T} = \frac{300K - 273K}{300K} = 0.09$$

(d) (7 Points) At the completion of the process, what is the total amount of heat Qc that was added to the ice?

at a given T

$$\epsilon(T) = \frac{\delta Q_H - \delta Q_c}{\delta Q_H} \qquad \epsilon(T) = 1 - \frac{\delta Q_c}{\delta Q_H}$$

$$\delta Q_c = \left[1 - \epsilon(T)\right] \delta Q_H = \left[1 - \left(1 - \frac{T_c}{T}\right)\right] \delta Q_H$$

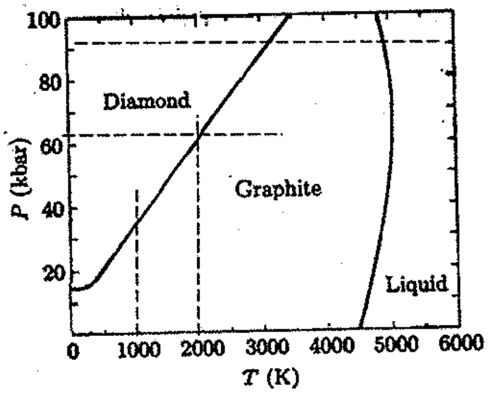
$$Q_c = \int_{373K}^{273K} \delta Q_c = \int_{373K}^{273K} dT \left(\frac{T_c}{T}\right)\left(m C_v^{H_2O}\right)$$

$$= T_c \, m \, C_v \ln \frac{273K}{373K}$$

$$= (273K)(1kg)\left(4200 \frac{J}{mol K}\right) \ln \frac{273K}{373K}$$

$$= \underline{\underline{3.6 \times 10^5 J}}$$

Problem 3 (30 Points)



The pressure P –temperature T phase diagram of carbon is shown here. The molar volume of graphite is $5.3\text{x}10^{-6}$ m^3 and the molar volume of diamond is $3.4\text{x}10^{-6}$ m^3, and you can assume that both are independent of temperature and pressure.

Note that 1 kbar=10^8 N/m^2.

a)(10 Points) Using the information in the phase diagram and in the statement of the problem, calculate the latent heat per mole L **(in Joules/mole)** for the solid-solid phase transformation at T=1000 K.

$$\frac{dP}{dT} = \frac{L}{T\Delta V} \qquad L = T\Delta V\,\frac{dP}{dT}$$

estimate $\frac{dP}{dT} \sim \frac{\Delta P}{\Delta T} \sim \frac{(62-35)\,\text{kbar}}{1000\,\text{K}} \times \frac{10^8\,N/m^2}{\text{kbar}} = 2.7\times10^6\,\frac{Nm^2}{K}$

$L = (1000K)(5.3 - 3.4)\times10^6 m^3\,(2.7\times10^6\,\frac{Nm^2}{K})$

= 5130 J/mole (depends on yr est for $\Delta P/\Delta T$)

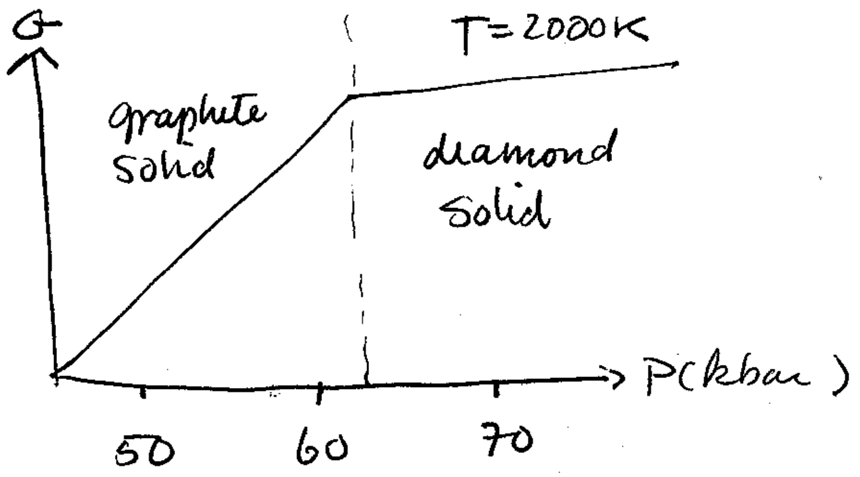
(b)(10 Points) Make a labeled and accurate sketch of the pressure dependence of the Gibbs free energy G at the constant temperature T=2000 K, for pressures P between 50 kbar and 70 kbar. Briefly explain the important features of your sketch.

$G = G(P,T,N)$ $\qquad dG = -SdT + VdP + \mu dN \sim VdP$

$\boxed{\frac{dG}{dP} \sim V}$

$V_{\text{diamond}} <$ V_{graphite}

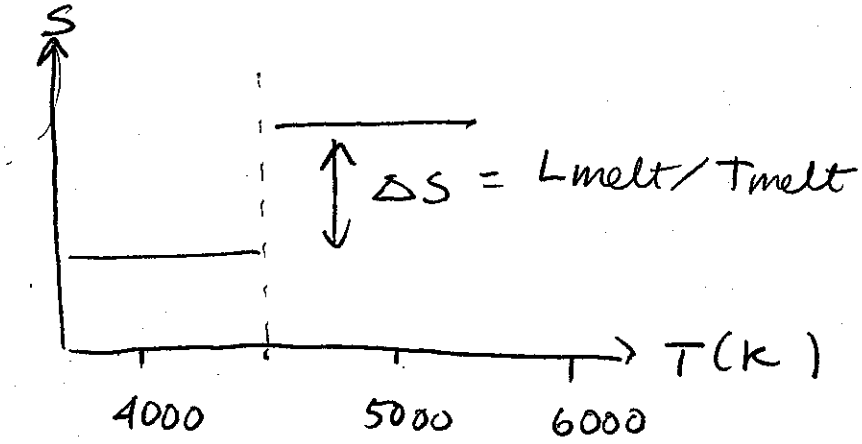
2000K: $P_c \cong 63$kbar



(c) (10 Points) Make a labeled and accurate sketch of the entropy per mole S at constant P=90 kbar, for temperatures between 4000 K and 5500 K. Briefly explain the important features of your sketch.

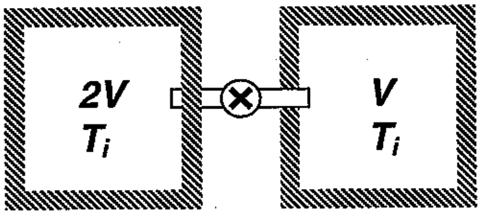
P = 90 kbar : diamond → graphite at ~3200 K

graphite solid → liquid at ~4500K $\equiv T_{melt}$



$S_{sol} < S_{liq}$ $\Delta S = \frac{L_{melt}}{T_{melt}}$

Problem 4 (20 Points)



We have two thermally insulated tanks with volumes V and 2V. Initially both tanks are at the same temperature T_i and each contains N moles of the same monatomic van der Waals gas, whose constants a and b are known. Then the valve which separates the two tanks is opened and the gas redistributes itself between the two tanks until equilibrium is reached.

Find an expression for the equilibrium temperature T_f.

Tanks are thermally isolated ; always have same U.

$$U^{vdw} = U^{ideal} - \frac{N^2 a}{V} = \frac{f}{2} N k_B T - \frac{N^2 a}{V} \qquad f \underline{\underline{= 3}}$$

Before: $$U_i = \left[\frac{3}{2} N k_B T_i - \frac{N^2 a}{V}\right] + \left[\frac{3}{2} N k_B T_i - \frac{N^2 a}{2V}\right]$$

After $$U_f = \frac{3}{2}(2N) k_B T_f - \frac{(2N)^2 a}{3V}$$

$$U_i = U_f$$

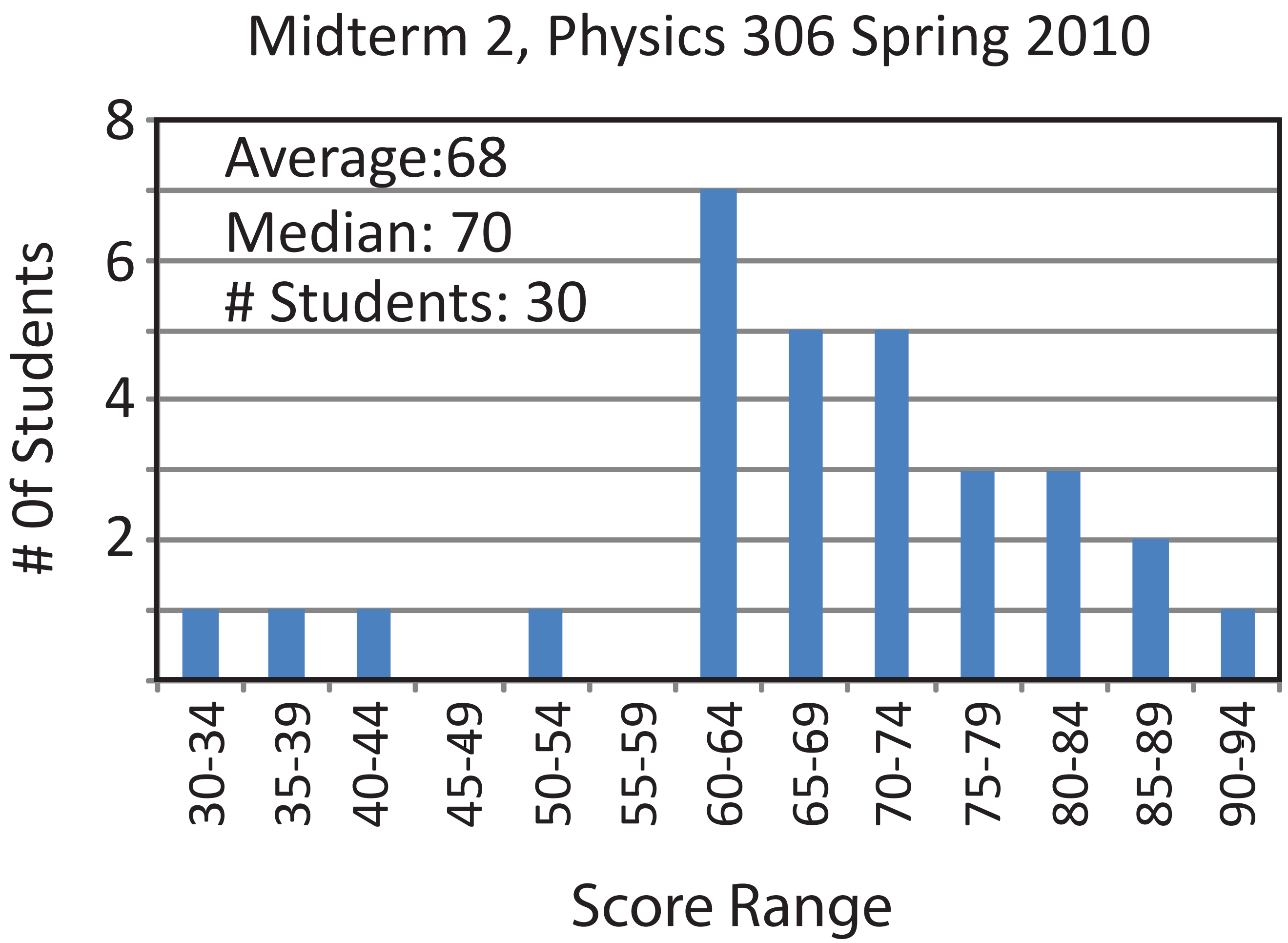
$$3 N k_B T_i - \frac{N^2 a}{V}\left(1 + \frac{1}{2}\right) = 3 k_B T_f N - \frac{4 N^2 a}{3V}$$

$$T_i - \frac{1}{2} \frac{N^2 a}{V N k_B} = T_f - \frac{4 N^2 a}{3V} \frac{1}{3 k_B N}$$

$$T_i - \frac{N a}{V k_B}\left(\frac{1}{2} - \frac{4}{9}\right) = T_f$$

$$T_i - \frac{N a}{V k_B}\left(\frac{9}{18} - \frac{8}{18}\right) = T_f$$

$$T_i - \frac{1}{18} \frac{N a}{V k_B} = T_f$$


Midterm 2, Physics 306 Spring 2010
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Median: 70
Students: 30
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6
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70-74
75-79
80-84
85-89
90-94
Score Range