Exam #2 for Physical Chemistry for Energy Science

Department of Nuclear Engineering, Seoul National University

5/23/07 Wednesday PM 2:30-4:00

90 min., closed book, one spike sheet (A4, one side), calculator, allowed.

TOTAL THREE PAGES INCLUDING A DATASHEET.

1. (30) Using $dG = -SdT + VdP + \mu dn$

1) Show that $\mu^v = \mu^l$ at a liquid-vapor equilibrium under constant temperature and pressure.

$dT = 0,\ dp = 0,\ dn = dn_v + dn_\ell = 0$

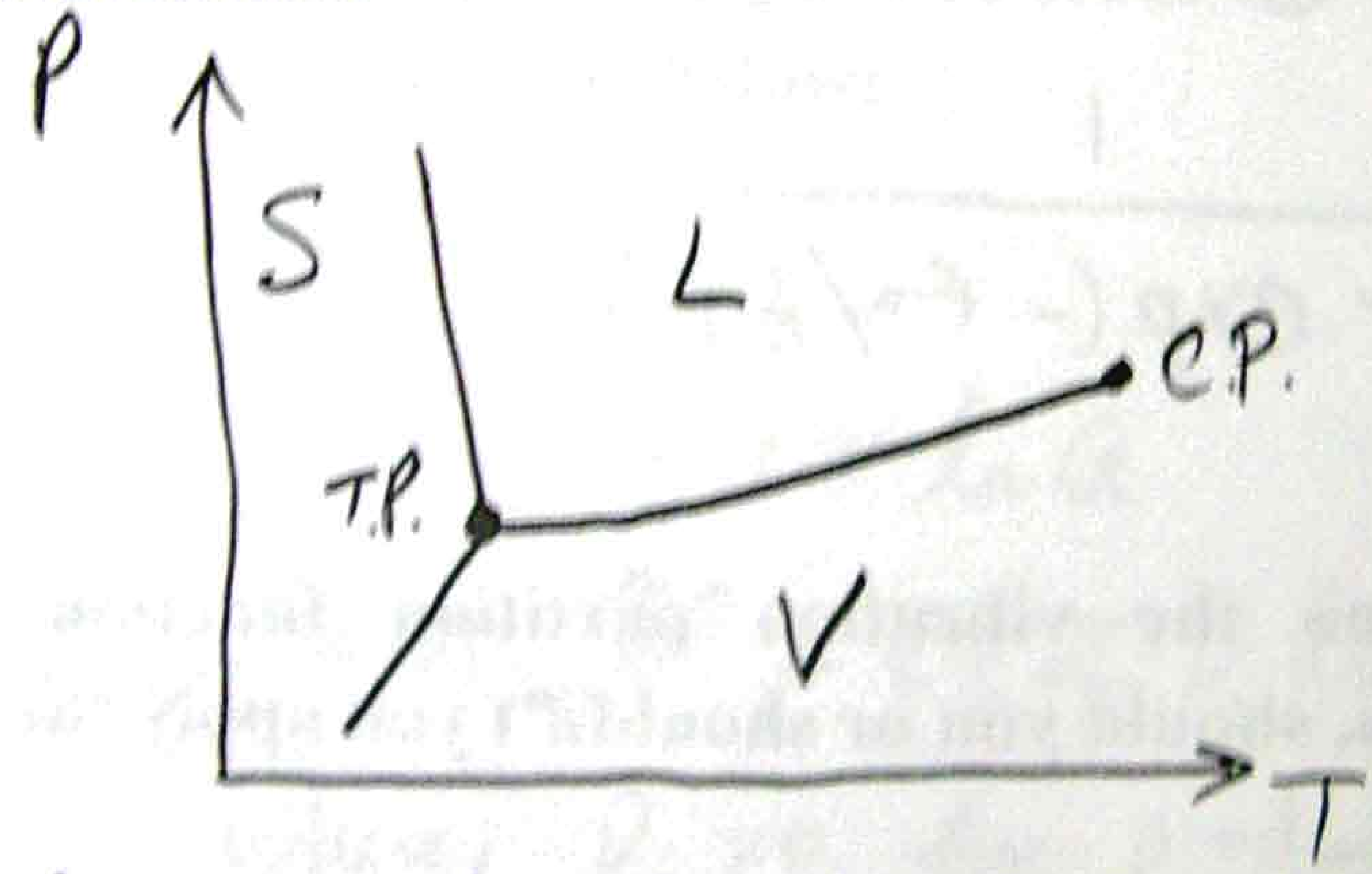
$\therefore\ dG_v = \mu_v dn_v$

$+)\ dG_\ell = \mu_\ell dn_\ell$

At equilibrium, $d(G_v + G_\ell) = \mu_v dn_v + \mu_\ell dn_\ell = \underline{(\mu_v - \mu_\ell) dn_v = 0}$

or $\underline{\mu_v = \mu_\ell \text{ at equilibrium}}$

2) For pure water, sketch phase boundaries of water in P-T coordinate.



$* \left(\Delta_f V_m = V_m^\ell - V_m^s < 0 \right.$ for water → negative slope for S-L boundary

3) Derive expression for the liquid-solid boundary in P-T coordinate.

$d\mu_\ell = -S_m^\ell dT + V_m^\ell dp$

$-)\ d\mu_s = -S_m^s dT + V_m^s dp$

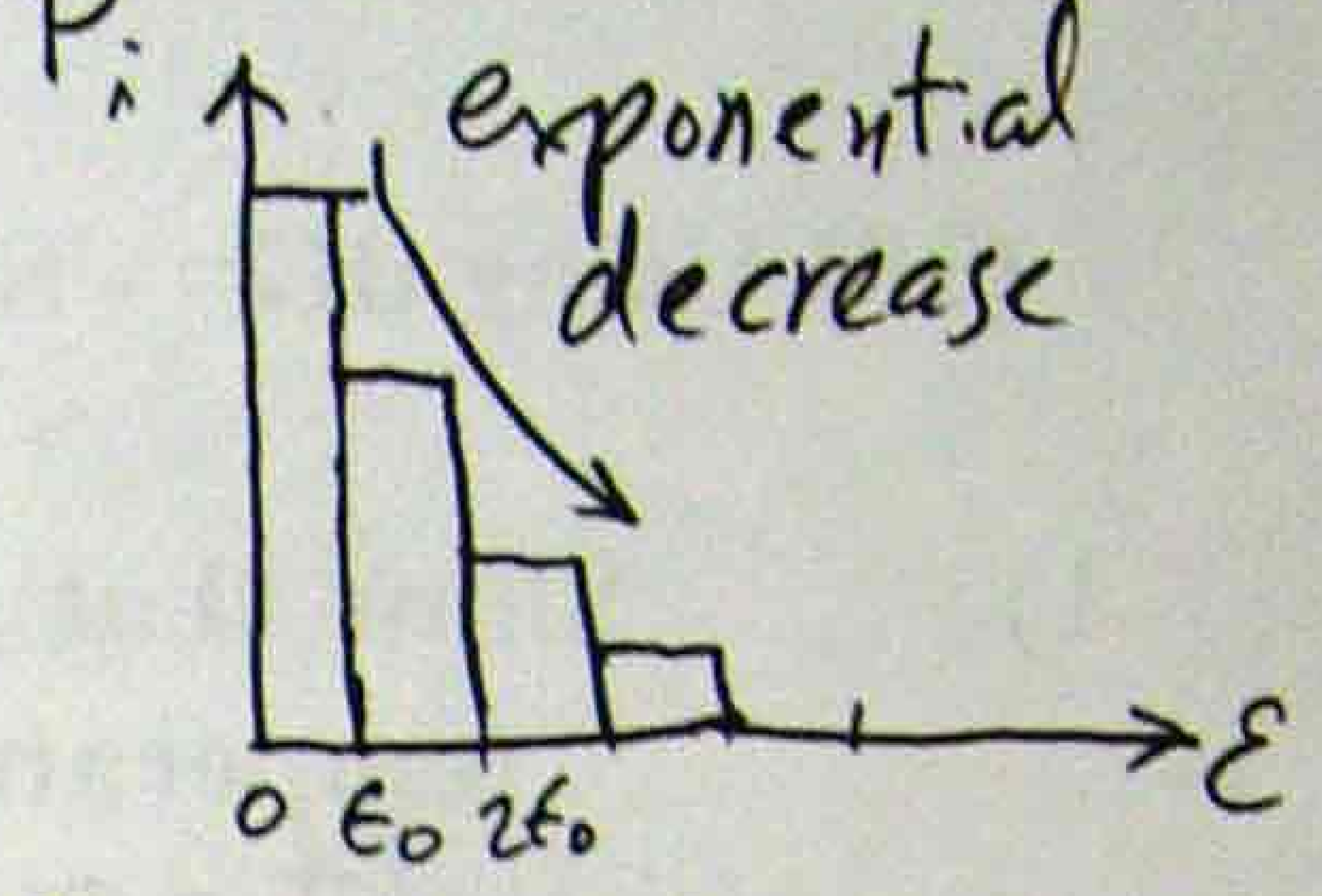
$d(\mu_\ell - \mu_s) = 0 \text{ (at boundary)} = (V_m^\ell - V_m^s)dp - (S_m^\ell - S_m^s)dT$

$$\therefore \frac{dp}{dT} = \frac{S_m^\ell - S_m^s}{V_m^\ell - V_m^s} = \frac{\Delta_f H_m}{T \Delta_f V_m} < 0$$

where $\Delta_f H_m$ (heat of fusion) > 0, $\Delta_f V_m < 0$

3. (40) Atoms in a single crystal are found to have vibration energy states that are separated by a constant difference, ε_o.

1) If the degeneracy at every state is single, sketch the population of atoms as function of the vibration energy.



$$\begin{pmatrix}\text{Population Probability} \\ \text{of } i\text{th state}\end{pmatrix} = P_i = \frac{N_i}{N} = \frac{e^{-\beta\cdot i\cdot\varepsilon_0}}{\sum_{i=0}^{\infty} e^{-\beta\cdot i\cdot\varepsilon_0}} = \frac{e^{-\beta\cdot i\cdot\varepsilon_0}}{\text{Constant}}$$

2) By neglecting both zero-point vibration and electronic energy, show that the partition function of the crystal is;

$$z = 1/[(1-\exp(-\varepsilon_o/kT)]$$

$$Z = \sum_{i=0}^{\infty} e^{-\beta\cdot i\cdot\varepsilon_0} = 1 + e^{-\beta\varepsilon_0} + e^{-2\beta\varepsilon_0} + \cdots = 1 + x + x^2 + \cdots = \frac{1}{1-x}$$

where $x = e^{-\beta\varepsilon_0}$; $\beta = 1/kT$

$$\therefore Z = \frac{1}{1-\exp(-\varepsilon_0/kT)}$$

3) In order to determine the vibration partition function for N indistinguishable atoms, should you or shouldn't you apply the factor, (1/N!)? Explain why.

Total Partition Function $Z_{tot} = Z_{tr} \cdot Z_{int} = Z_{tr} \cdot Z_{vib} \cdot Z_{rot} Z_{elec}$.
The internal d.o.f. is evaluated for one specific atom that is already distinguished! "No (1/N!) applied."
(For translation, $Z_{tr}^{(1)}$ is obtained for one typical atom.
But there are N indistinguishable atoms, $Z_{tr} = \frac{(Z_{tr}^{(1)})^N}{N!}$)

4) Once you have determined the partition function, how would you determine thermodynamic energy including U, H, and G? Assume that electronic energy is negligible.

$Z_{tot} = \frac{Z_{tr}^{(1)}}{L} Z_{vib} Z_{rot}$, by neglecting Z_{elec}.

Then

$$U_m = \frac{RT^2}{Z_{tot}} \frac{\partial Z_{tot}}{\partial T} + U_{m0}$$ neglect zero-point vibration.

$$H_m = U_m + PV_m \; (= U_m + RT \text{ if IG})$$

$$G_m = -RT \ln\left(\frac{Z_{tr}^{(1)}}{L} Z_{vib} Z_{rot}\right) + \cancel{U_{m0}} \to 0$$

$$S_m = R \ln\left(\frac{Z_{tr}^{(1)}}{L} Z_{vib} \cdot Z_{rot}\right) + R + \frac{U_m - \overset{\to 0}{\cancel{U_{m0}}}}{T}$$

Note: In solids usually vibration and electric energies are important.

5. **(30) For** $CO(g)+\frac{1}{2}O_2(g)=CO_2(g)$.

1) Derive the Van't Hoff Equation from the first principles for all chemical reactions, as below;

$\Delta_{rxn} G^0 = -RT \ln K_a$

$$\mu = \mu^\theta(T) + RT \ln a$$

$$\Delta_{rxn} G = \Delta_{rxn} G^\theta + RT \sum_i \nu_i \ln a_i = \sum_i \nu_i \mu_i^\theta + RT \ln\left(\prod_i a_i^{\nu_i}\right)$$

Where $\nu_i > 0$ for products
$\nu_i < 0$ for reactants

At equilibrium, $\Delta_{rxn} G = 0$

$$\therefore \Delta_{rxn} G^\theta = -RT \ln\left(\prod_i a_i^{\nu_i}\right) = -RT \ln K_a$$

Where $K_a = \prod_i a_i^{\nu_i}$

Finally, $\underline{\Delta_{rxn} G^\theta = -RT \ln K_a}$

2) Under the standard state and the reaction was made isothermally at 25 °C, assume that the initial reactant mixture contains a 4:1 ratio of CO and oxygen. $\Delta_f G^0$ is zero for oxygen gas at the standard state and 25 °C. What is the mole fraction of CO2 at equilibrium, if fugacity coefficient is 0.9 for all gases?

$$\Delta_{rxn} G^\circ = \Delta_f G^\circ_{CO_2} - \Delta_f G^\circ_{CO} - \frac{1}{2}\Delta_f G^\circ_{O_2} = -394.36 + 137.17 + 0 \ \frac{kJ}{mole}$$

$$= -257 \ kJ/mole$$

$$K_a = \exp\left[-\frac{\Delta_{rxn} G^\circ}{RT}\right] = e^{\left[\frac{257{,}000 \ J/mole}{(8.314 \ J/mole\,K)(298K)}\right]} = e^{103.7} \sim \infty$$

$$= \frac{\phi P_{CO_2}/P^\circ}{(\phi P_{CO}/P^\circ)(\phi P_{O_2}/P^\circ)^{1/2}} = 1.054 \frac{X_{CO_2}}{X_{CO}\sqrt{X_{O_2}}}$$

i	n_{i0}	ν_i	n_{if}	n_{if}	x_{if}
CO	$4m$	-1	$4m-\alpha$	$\sim 2m$	0.5
O_2	m	$-\frac{1}{2}$	$m-\frac{\alpha}{2}$	$\rightarrow$ <u>Smallest</u> ~ 0 $(\alpha \cong 2m)$	0
CO_2	0	$+1$	α	$\sim 2m$	0.5
				$n_f(tot) = 4m$	1.0

$$\therefore \underline{X_{CO_2} = 0.5}$$

3) Under the standard state, explain and sketch how $\Delta_{rxn} G^0$ of the reaction will vary as function of reaction temperature.

$$\Delta_{rxn} G^\circ = \Delta_{rxn} H^\circ - T\Delta_{rxn} S^\circ$$

In general, $\Delta_{rxn} H^\circ$ is a weak function of T.

$\Delta_{rxn} S^\circ$ is governed by the gases.

$$\Delta_{rxn} S^\circ = \begin{cases} >0 & \text{if the \# of gas moles increases} \\ =0 & \text{〃 〃 is constant} \\ <0 & \text{〃 〃 decreases} \end{cases}$$

For $CO + \frac{1}{2}O_2 = CO_2$

1 mole + $\frac{1}{2}$ mole → 1 mole

$\therefore \Delta_{rxn} S^\circ < 0$ $\therefore$