Chemistry 230
Problem Set # 10 -- Answers

1. This problem is like Problem 2 on PS 9, but with the inclusion of the correction for real gas behavior in part (b). See Problems 7.44 and 8.27 in Levine (except use 23.7$\underline{5}$6 torr). One obtains 8557 J/mol, which agrees with the result from tabulated data in the appendix.

2. (a) a = 3.61 L^2 atm mol^{-2}; b = 0.0429 L/mol.
   (b) $H_{m,id} - H_m$ = 25.2 J/mol; $S_{m,id} - S_m$ = 0.0495 J mol^{-1} K^{-1}; $G_{m,id} - G_m$ = 10.47 J/mol.

3. $\ln \varphi_P = \int_0^P \left[\frac{V_m}{RT} - \frac{1}{P'} \right] dP'$. One must first compute from the experimental data the integrand (the quantity in square brackets) and plot it *vs*. P'. Then one must integrate it to the desired final P.
   (a) A least-squares fit of the integrand gives: [ ] = –0.0036 + 4.1135E-06 P – 5.9313E-08 P^2.
   Integration yields ln φ = –0.1486 at P = 40 atm φ_{40} = 0.862 and f_{40} = 34.5 atm.
   At P = 90 atm, φ_{90} = 0.701 and f_{90} = 63.1 atm.
   (b) 40 atm: P_r = 40/72.8 = 0.549; T_r = 333/304.2 = 1.095 $\varphi_{40} \approx$ 0.93 and f_{40} = 37 atm.
   90 atm: P_r = 90/72.8 = 1.236 $\varphi_{90} \approx$ 0.85 and f_{90} = 76 atm.
   (c) Using the a and b values from Problem 2 above, together with the results from Problem 10.43 in Levine, we obtain: φ_{40} = 0.872 and f_{40} = 34.9 atm; φ_{90} = 0.721 and f_{90} = 64.9 atm.

4. (a) ΔH° = –48.9 kJ/mol; ΔG°_{1000} = –66.6 kJ/mol; ΔS° = 17.6$_9$ J mol^{-1} K^{-1}.
   (b) With only three points it is really hard to decide whether any deviation from the straight line is real or simply due to experimental uncertainty. The values obtained in Part (a) were based on the assumption of linearity in the van't Hoff plot, which is equivalent to assuming that ΔH° and ΔS° are independent of T. If we believe the deviation from linearity is real, then the slight upward curvature means that $|\Delta H^\circ|$ is less at large T (small 1/T) than at small T. Since ΔH° is also <u>negative</u>, this means it is <u>larger</u> (more positive) at large T, which in turn means that $\Delta C_P > 0$.
   (c) $Q \approx P_{CO_2} / P_{CO}$ = 4 << K°, so the reaction must proceed to the right. This is <u>reduction</u> of NiO.

5. $K^\circ = \frac{a(CaO)\ a(CO_2)}{a(CaCO_3)}$. For solids $\ln a \approx V_m \frac{\Delta P}{RT}$. At the indicated P and T this yields $a(CaCO_3)$ = 1.48 and a(CaO) = 1.19. For CO_2 @ 1115 atm and 1273 K, P_r = 15.3 and T_r = 4.18 $\varphi \approx$ 1.11. Using K° = 4.5 and solving for P_{CO_2} we obtain 5.0 bar, which is about 10% larger than would be obtained without the large added pressure of Ar. (In this case there is substantial cancellation of the pressure effects on the two sides of the equation.)