Thermodynamics. Problems. Sheet 5.

1. Recall that material equilibrium between two systems exists when there is zero material transfer between them. Are the following composite systems in material equilibrium with their surroundings?

a) Water in a glass at ambient temperature	f) Ice cubes in the freezer (no-frost freezer).
b) Water in a closed bottle.	g) Snow on a mountain.
c) Water in an open bottle.	h) Sea water.
d) Water in our bodies.	i) Water vapor in a bubble inside Antarctic ice.
e) Hot coffee in a high-quality thermos.	j) Carbon dioxide in a cola beverage before and after opening it.

2. Compute the heat of vaporization of 1g of ethylamine from the following data.

T (ºC)	**P (mmHg)**
-22.9	111.2
-13.9	183
-5.6	281.8
5.8	481.3
16.2	750.5

[Answer: 652 J]

3. The vapor pressure of 1 mole of a certain ketone is given in the following table:

T (ºC)	**P (Torr)**
57.4	1.00
100.4	10.0
133.0	40.0
157.3	100
203.5	400
227.5	760

a) Which is the normal boiling point?
b) Which is the enthalpy of vaporization of the ketone?

Use degrees Kelvin. 1 Torr = 133.322 Pa.

[Answer: a) 227.5 K; b) 53.6 kJ/mol]

4. In a temperature range close to the transition from orthorhombic sulfur to monocline sulfur, S_{8_ortho} (s) = S_{8_monocl} (s), vapor pressures can be expressed by the following equations:

   $\log P_{ortho} = -5267\ T^{-1} + 11.866$
   $\log P_{monocl} = -5082\ T^{-1} + 11.364$
   (T given in K, vapor pressures in mmHg)

   Compute the temperature and the enthalpy at the transition.
   Clarification: They ask for the temperature of coexistence of the three phases (the two solid phases and the vapor), and the enthalpy of transition from one solid phase to the other.

   [Answer: 368.5 K; 3.54 kJ/mol]

5. At 0ºC and 1.00 atm, the molar volume of water is 18.018 cm^3 and that of ice is 19.64 cm^3. How would the melting point shift if the pressure was increased to 3.00 atm? The melting heat of ice is 79.69 cal/g.

   [Answer: –0.015 K]

6. Trouton's rule states that the entropy of vaporization of most liquids is approximately equal to 21.5 cal/(K·mol), at boiling temperature and pressure of 1 atm. Compute by means of an approximate expression the change in the point boiling resulting from a drop in the pressure from 760 to 750 mmHg, for toluene, whose normal boiling point is 110.6ºC.

   [Answer: –0.47 K]

7. Compute the pressure required to melt 1.00 g of ice at a temperature of -1ºC, knowing that its heat of melting is 79.69 cal/g. The density of ice is 0.92 g/cm^3 and that of liquid water is 1.00 g/cm^3.

   [Answer: 139 atm]

8. The vapor pressure of benzene at 21ºC is 76 Torr and its normal temperature of boiling point is 80ºC. Compute the enthalpy of vaporization explaining the approximations used.

   [Answer: 33.7 kJ/mol]

9. Over a wide temperature range, the vapor pressures (in mmHg) of solid and liquid UF_6 follow the approximate equations:

   $\log P_S = 10.648 - 2559.5\ T^{-1}$, and

   $\log P_L = 7.5396 - 1511.3\ T^{-1}$.

   a) At what condition of temperature and pressure can solid, liquid and gas UF_6 coexist in equilibrium?
   b) At which temperature is UF_6 in equilibrium with its vapor at 1 atm? At this condition, is the condensed phase solid or liquid?

   [Answer: a) 337 K; 1.50 atm; b) 329 K; solid]

10. In a temperature range close to the triple point of $TaBr_5$, the vapor pressures (in mmHg) of the solid and the liquid follow the following equations:

$\log P_S = 12{,}571 - 5650\ T^{-1}$, and

$\log P_L = 8{,}171 - 3265\ T^{-1}$.

Compute for $TaBr_5$

a) the triple point and ΔH of melting, and
b) the boiling point and the entropy of evaporation.

[Answer: a) 542 K; 4.57×10^4 J/mol; b) 617 K; 101.3 J/K mol]

11. The melting heat of naphthalene at the normal melting point of 80.0ºC is 36.0 cal/g. Compute the change in the melting point when the pressure increases by 1 atm, knowing that the density of solid naphthalene is 1.145 g/cm^3 and that of liquid naphthalene is 0.981 g/cm^3.

[Answer: +0.035 K]