Problems - Chapter 12 (with solutions)

1) (7.23) Explain the term <u>polarizability</u>. What kind of molecules tend to have high polarizabilities? What is the relationship between polarizability and intermoleular forces?

Polarizability refers to the shift in electron density in an atom or molecule when it is brought close to a charge (positive attracts, negative repels).

Larger molecules and molecules where the outermost electrons are further away from the nucleus tend to be the ones that are most easily polarized. So, for example, Xe is more polarizable than He, and C_2Cl_6 is more polarizable than CCl_4.

Polarizability is most important for molecules attracted to one another by dispersion forces. It is also important for "mixed" forces of attraction, such as ion-molecule or dipole-molecule attractive forces.

2) (7.107) Which of the following substances has the highest polarizability: CH_4, H_2, CCl_4, SF_6, H_2S?

Generally speaking polarizability is higher for larger molecules, and molecules with valence electrons far away from the atomic nuclei. So I would expect

$CCl_4 > SF_6 > H_2S > CH_4 > H_2$

3) (7.34) Arrange the following in order of increasing boiling point: RbF, CO_2, CH_3OH, CH_3Br. Explain your reasoning.

Highest to lowest   RbF $> CH_3OH > CH_3Br > CO_2$
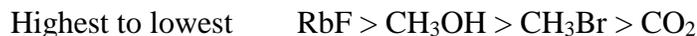
RbF is ionically bonded, and so should have a very high value for boiling point. CO_2 is nonpolar (and so only experiences dispersion forces) and so should have a low boiling point (and in fact is a gas at room temperature). Both CH_3OH and CH_3Br are polar, but CH_3OH can form hydrogen bonds between molecules, which is likely more important than the fact that CH_3Br has the larger value for molecular mass.

4) (7.36) Which member of each of the following pairs of substances would you expect to have a higher boiling point? Explain your answers.

a) O_2 or Cl_2 Both are nonpolar, but Cl_2 is larger and so should have stronger dispersion forces between molecules, and so a higher boiling point.

b) SO_2 or CO_2 SO_2 is nonlinear (trigonal planar electron cloud geometry) and so polar, and it also has a larger molecular mass than CO_2, which is linear and so nonpolar. Both of these factors favor SO_2 as having a higher boiling point.

c) HF or HI   HF molecules can hydrogen bond to one another, and so HF likely has a higher boiling point than HI, even though HI is larger and so has stronger dispersion forces.

5) (7.38) Explain the following in terms of intermolecular forces.

a) NH_3 has a higher boiling point than CH_4 The molecules are about the same size and molecular mass, but NH_3 is polar, and NH_3 molecules can hydrogen bond to one another, while CH_4 is nonpolar.

b) KCl has a higher melting point than I_2 The bonding in KCl is ionic, so KCl should have a high value for melting point. I_2 is nonpolar, and the attractive forces between molecules are relatively weak dispersion forces, and so I_2 should have a lower melting point.

6) (12.1) Explain why liquids, unlike gases, are nearly incompressible.

The molecules in a liquid are in close contact with one another, so it takes a large pressure to force the molecules even a little bit closer together. Gases are mostly empty space, and so while increasing the pressure decreases the average distance between gas molecules, the molecules are still not generally in close contact.

7) (12.12) The vapor pressure of benzene (C_6H_6) is 40.1 mm Hg at 7.6 °C. What is the vapor pressure at 60.6 °C? The molar heat of vaporization for benzene is 31.0 kJ/mol.

We can use a form of the Clausius-Clapeyron equation (eq 12.4 of Burdge)

$$\ln(p_2/p_1) = - (\Delta H°_{vap}/R) [(1/T_2) - (1/T_1)]$$

Let $T_1 = 7.6$ °C = 280.8 K $T_2 = 60.6$ °C = 333.8 K
$p_1 = 40.1$ mm Hg

Then

$$\ln(p_2/p_1) = - [(31000. \text{ J/mol·K})/(8.314 \text{ J/mol·K})] [(1/333.8 \text{ K}) - (1/280.8 \text{ K})]$$

$$= 2.108$$

Taking the inverse ln of both sides of this equation

$$(p_2/p_1) = e^{2.108} = 8.235$$

$$p_2 = p_1 e^{2.108} = (40.1 \text{ mm Hg})(8.235) = 330. \text{ mm Hg} = 330. \text{ torr}$$

8) (12.16) Vapor pressure measurements for mercury at several different temperatures are given below. Plot this data in an appropriate way, and determine the molar enthalpy of vaporization for mercury.

T (°C)	200.0	250.0	300.0	320.0	340.0
p (mm Hg)	17.3	74.4	246.8	376.3	557.9

We may use the form of the Clausius-Clapeyron equation in eq 12.1 of Burdge to analyze this data. We plot ln p vs (1/T). The slope of the line obtained from the plot is equal to - (ΔH°_{vap}/R), from which we can find ΔH°_{vap}.

T (°C)	p (torr)	T (K)	1/T (K^{-1})	ln p
200.0	17.3	473.2	0.002113	2.8507
250.0	74.4	523.2	0.001911	4.3095
300.0	246.8	573.2	0.001745	5.5086
320.0	376.3	593.2	0.001686	5.9304
340.0	557.9	613.2	0.001631	6.3242

The data are plotted below (using EXCEL, which was also used to find the parameters for the best fitting line).
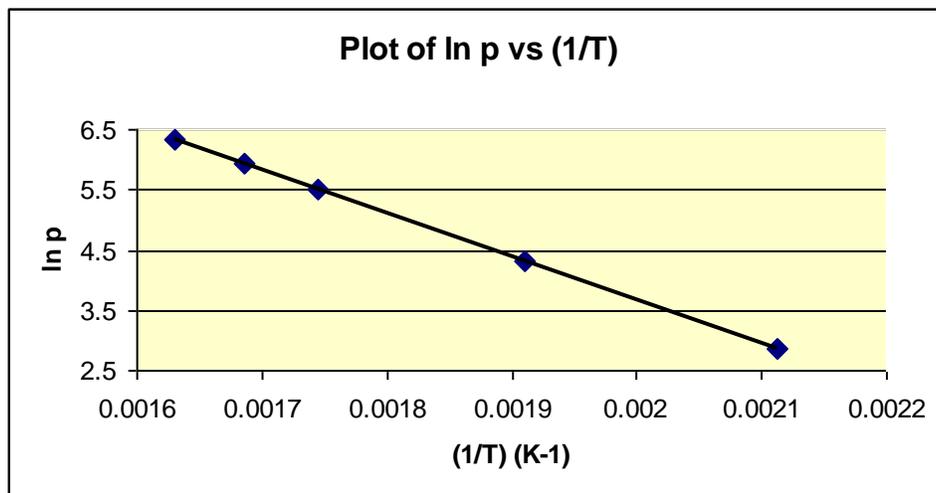
Based on the plot, I get

m = slope = - 7210. K ΔH°_{vap} = - mR = - (- 7210. K) (8.314 J/mol·K)

= 59.9 kJ/mol

9) (12.18) What is an <u>amorphous solid</u>? How does it differ from a crystalline solid?

An amorphous solid is a solid that does not have a regular arrangement of the particles making up the solid, that is, there is no repeating crystal structure such as exists in crystalline solids.

10) (12.50) How is the molar heat of sublimation related to the molar heat of fusion and the molar heat of vaporization? On what law is this relationshop based?

Since $s \rightarrow g = s \rightarrow \ell + \ell \rightarrow g$

We would expect, based on Hess' law, that

$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$

The above expression is only approximately correct if we use the usual values for ΔH for each of the phase transitions, because the enthalpy changes for different phase transitions are usually measured at different temperatures and pressures (for example, the enthalpy of fusion for water is usually given at 1 atm and 0. °C, while the enthalpy of vaporization is usually given at 1 atm and 100. °C).

11) (12.55) What is the <u>critical temperature</u>? What is the significance of the critical temperature in terms of the condensation of gases?

The critical temperature is defined as the temperature above which an isothermal (constant temperature) compression of a gas will never lead to a phase trase transition or formation of a liquid.

What this means is that if we have a gas at a temperature below the critical temperature we can liquefy the gas by increasing the applied pressure. We make use of this in refrigerators and air conditioners, which contain working fluids that can be liquified by compression.

12) (12.64) Calculate the amount of heat (in kJ) required to convert 150.2 g of water into steam at T = 100. °C. Note that for water at 100.0 °C, $\Delta H°_{vap} = 40.7$ kJ/mol.

M(H_2O) = 18.01 g/mol, and so the moles of water is

$n = 150.2$ g $\dfrac{1 \text{ mol}}{18.02 \text{ g}} = 8.335$ mol

So $q = (8.335 \text{ mol}) (40.7 \text{ kJ/mol}) = 339.$ kJ