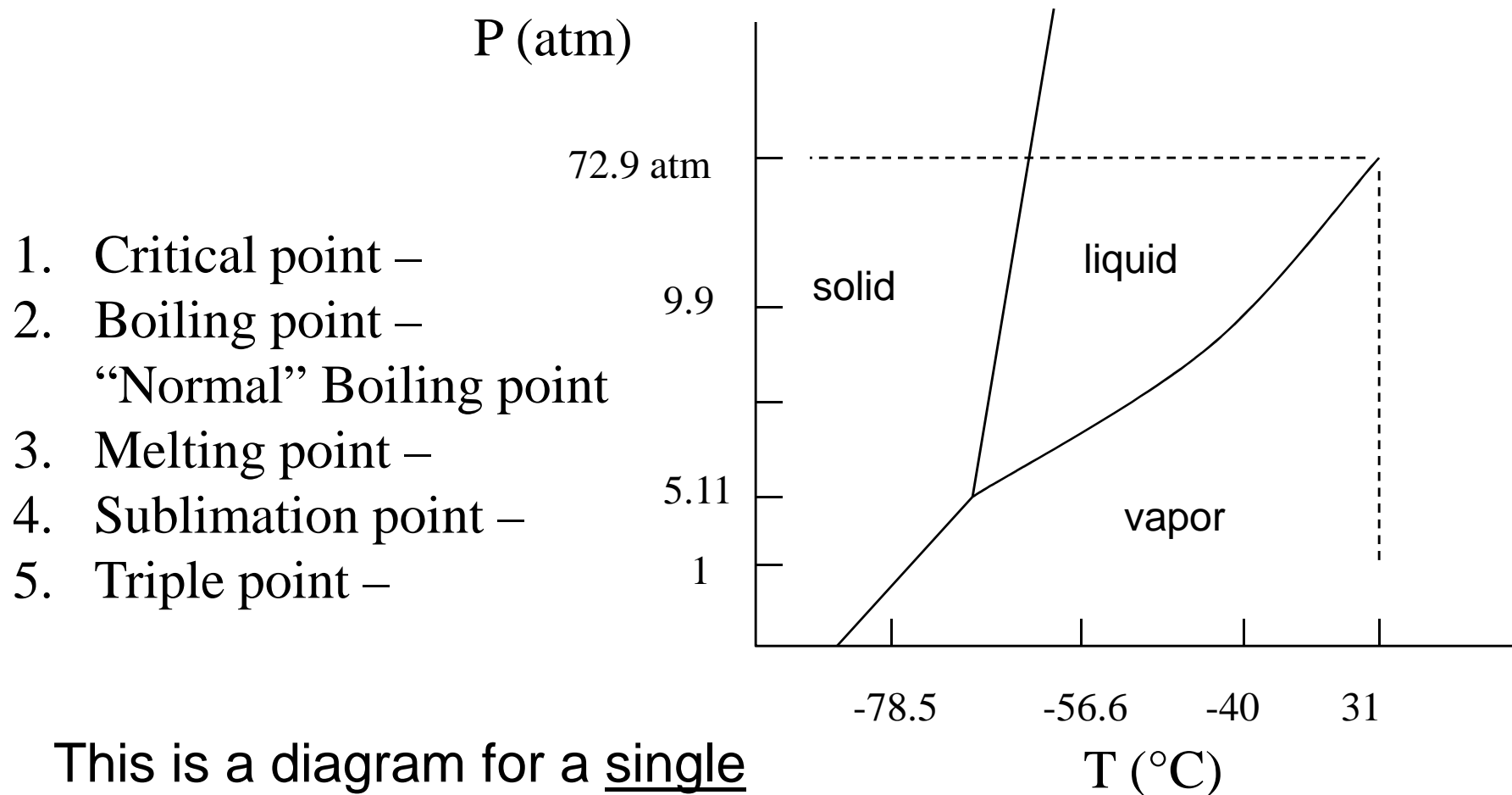# ABE 201
Biological Thermodynamics 1

Module 8:

Phase Equilibria

Outline

- Phases of matter and terminology

- Relationships between phase and other state properties (T, P, etc.)

- Methods of determining these relationships

Phases of Mater

P (atm)

1. Critical point –
2. Boiling point –
   "Normal" Boiling point
3. Melting point –
4. Sublimation point –
5. Triple point –

72.9 atm

9.9

5.11

1

solid

liquid

vapor

-78.5   -56.6   -40   31

T (°C)

This is a diagram for a <u>single</u> substance at <u>equilibrium.</u>

Gas vs. Vapor

Gases cannot take the physical form of liquids, they exist in only one phase.

Vapors can be condensed by compressing or cooling to form liquids.

Vapors can be condensed, Gases cannot !!

Vapor vs. Gas

- There is no limit to the "amount" of a <u>gas</u> there is in the gas phase

$$0 \leq p_{O2} \leq \text{infinity}$$

- The **is** an upper limit to the "amount" of a <u>vapor</u> that can exist in the gas phase

$$0 \leq p_{H2O} \leq p^*_{H2O}$$

This limit is called the
saturation vapor pressure of water.

Saturation Vapor Pressure

- Vapor pressure is a physical property, and does NOT depend on overall pressure.

- It DOES depend on TEMPERATURE, however.

- Vapor pressure of a species is a measure of its *volatility*

    - *If vapor pressure for A is higher than for B, which is more volatile?*

Relationship of Partial and Saturation Vapor Pressures

- Partial pressure describes the relative amount of vapor in a mixture.

- Saturation vapor pressure describes the maximum amount of vapor that can exist at a certain temperature.

- If a gas and a liquid are in equilibrium with each other, the liquid vapor in the gas is saturated and its partial pressure equals the vapor pressure at that temperature.

Partial and Vapor Relationship ... (cont'd)

- If the partial pressure is equal to the vapor pressure, the mixture is called *saturated* in the vapor material.

$$p_A = \frac{n_A}{n} = p_A^*$$

Determining Saturation Vapor Pressure

- Look up value(s) in table, interpolate between values if necessary
  - <u>Perry's Handbook of Chemical Engineering</u>
  - <u>CRC Handbook of Chem. & Phys</u>
  - Table B.3 has vapor pressure data for water
- Use Clausius-Clapeyron equation for more accurate "interpolation"
- Use Antoine equation and empirical constants

Table B.3 Vapor Pressure of Water[a]

p_v(mm Hg) versus T (°C)

Example: The vapor pressure of liquid water at 4.3°C is 6.230 mm Hg

T(°C)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	4.579	4.613	4.647	4.681	4.715	4.750	4.785	4.820	4.855	4.890
1	4.926	4.962	4.998	5.034	5.070	5.107	5.144	5.181	5.219	5.256
2	5.294	5.332	5.370	5.408	5.447	5.486	5.525	5.565	5.605	5.645
3	5.685	5.725	5.766	5.807	5.848	5.889	5.931	5.973	6.015	6.058
4	6.101	6.144	6.187	6.230	6.274	6.318	6.363	6.408	6.453	6.498
5	6.543	6.589	6.635	6.681	6.728	6.775	6.822	6.869	6.917	6.965
6	7.013	7.062	7.111	7.160	7.209	7.259	7.309	7.360	7.411	7.462
7	7.513	7.565	7.617	7.669	7.722	7.775	7.828	7.882	7.936	7.990
8	8.045	8.100	8.155	8.211	8.267	8.323	8.380	8.437	8.494	8.551
9	8.609	8.668	8.727	8.786	8.845	8.905	8.965	9.025	9.086	9.147
10	9.209	9.271	9.333	9.395	9.458	9.521	9.585	9.649	9.714	9.779
11	9.844	9.910	9.976	10.042	10.109	10.176	10.244	10.312	10.380	10.449
12	10.518	10.588	10.658	10.728	10.799	10.870	10.941	11.013	11.085	11.158
13	11.231	11.305	11.379	11.453	11.528	11.604	11.680	11.756	11.833	11.910
14	11.987	12.065	12.144	12.223	12.302	12.382	12.462	12.543	12.624	12.706
15	12.788	12.870	12.953	13.037	13.121	13.205	13.290	13.375	13.461	13.547
16	13.634	13.721	13.809	13.898	13.987	14.076	14.166	14.256	14.347	14.438
17	14.530	14.622	14.715	14.809	14.903	14.997	15.092	15.188	15.284	15.380
18	15.477	15.575	15.673	15.772	15.871	15.971	16.771	16.171	16.272	16.374
19	16.477	16.581	16.685	16.789	16.894	16.999	17.105	17.212	17.319	17.427
20	17.535	17.644	17.753	17.863	17.974	18.085	18.197	18.309	18.422	18.536
21	18.650	18.765	18.880	18.996	19.113	19.231	19.349	19.468	19.587	19.707

Liquid water

Clausius-Clapeyron Equation

- Use tabulated vapor pressures to estimate vapor pressure for non-tabulated values.

- Similar to interpolation, but more accurate in predicting vapor pressure

- Semi-theoretical: relates vapor pressure to heat of vaporization (also related to volatility)

$$\ln p^* = -\frac{\Delta \hat{H}_V}{RT} + B$$

Look up values for p* at known T's – calculate heat of vaporization then fit equation to find B

Empirical Equation

Antoine Equation

• Empirically derived relationship

$\log_{10} (p^*) = A - B/(C + T)$ p^* = vapor pressure (mm Hg)

   T = temperature (^{o}C)

   A, B, C = constants

Table B.4

COMPOUND	RANGE (^{o}C)	A	B	C
Acetic Acid	0 to 36	7.18807	1416.7	225
Ammonia	-83 to 60	7.55466	1002.711	247.885
Ethanol	19.6 to 93.4	8.11220	1592.864	226.184
Water	0 to 60	8.10765	1750.286	235.000
Water	60 to 150	7.96681	1668.210	228.000

Summary

- Phase is a state property that can be related to other state properties (T, P, etc.)

- Phase property relationships are usually based on thermodynamic equilibrium

- Vapor/liquid systems in real application are often <u>not</u> at equilibrium, but equilibrium relationships are useful for predicting behavior