Extensive/intensive (Schroeder 5.2) If you consider two identical systems taken together (e.g. two cups of water, or two identical cubes of metal), each thermodynamic property either doubles or remains the same.

Extensive An extensive property, such as mass will double when you've got twice as much stuff.

Intensive An intensive property, such as density will be the same regardless of how much stuff you've got.

We care about extensivity and intensivity for several reasons. In one sense it functions like dimensions as a way to check our work. In another sense, it is a fundamental aspect of each measurable property, and once you are accustomed to this, you will feel very uncomfortable if you don't know whether it is extensive or intensive.

How to measure things I may give you questions which require you to make use of these definitions.

Volume Measure dimensions and compute it. *(extensive)*

Pressure Force per area. Can equalize if systems can exchange volume. *(intensive)* (Schroeder 1.2)

Temperature Find something that depends on temperature, and calibrate it. Alternatively use an ideal gas. Equalizes when systems are in contact. *(intensive)*

Energy Challenging... measure work and heat (e.g. by measuring power into resistor) and use the First Law. *(extensive)*

$$W = -\int p dV \tag{1}$$

Entropy *(extensive)* Measure heat for a quasistatic process and find

$$\Delta S = \int \frac{đQ}{T} \tag{2}$$

(Schroeder 3.2)

Derivatives Measure changes of one thing as the other changes, with the right stuff held fixed.

First Law (Energy conservation, Schroeder 1.4)

$$dU = đQ + đW \tag{3}$$

Second Law (Entropy increases, Schroeder 2.3)

$$\Delta S_{\text{system}} + \Delta S_{\text{environment}} \geq 0 \tag{4}$$

Thermodynamic identity (Schroeder 3.4)

$$dU = TdS - pdV \tag{5}$$

Total differentials When we have a total differential, the things in front of the dS, dV, etc are partial derivatives.

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad -p = \left(\frac{\partial U}{\partial V}\right)_S \tag{6}$$

Also, you can integrate along a path using a total differential, and can do linear algebra using total differential equations, e.g. substituting one for another. Fun example:

$$dS = \frac{1}{T}dU + \frac{p}{T}dV \tag{7}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V \qquad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_U \tag{8}$$

(the second derivative shown here is known as the cyclic chain rule in a more general sense)

Thermodynamic potentials (Schroeder 1.6, 5.1)

Helmholtz free energy

$$F = U - TS \tag{9}$$

$$dF = dU - TdS - SdT \tag{10}$$

$$= -SdT - pdV \tag{11}$$

Enthalpy

$$H = U + pV \tag{12}$$

$$dH = dU + pdV + Vdp \tag{13}$$

$$= TdS + Vdp \tag{14}$$

Gibbs free energy

$$G = H - TS \tag{15}$$

$$= U - TS + pV \tag{16}$$

$$dG = dH - TdS - SdT \tag{17}$$

$$= -SdT + Vdp \tag{18}$$

Maxwell relations You should be able to use the fact that mixed partial derivatives do not depend on the order taken to find Maxwell relations. Also using the differentials above, e.g.

$$\left(\frac{\partial\left(\frac{\partial G}{\partial T}\right)_p}{\partial p}\right)_T = \left(\frac{\partial\left(\frac{\partial G}{\partial p}\right)_T}{\partial T}\right)_p \tag{19}$$

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \tag{20}$$

Statistical entropy (Schroeder 2.6, Problem 6.43) Boltzmann formulation (microcanonical or for large N):

$$S(E) = k_B \ln g(E) \tag{21}$$

where g is the number of microstates (or energy eigenstates). We spent little time on the Boltzmann formulation, but it is helpful to know that at sufficiently high temperatures the entropy approaches k_B times the logarithm of the number of energy eigenstates.

Gibbs formulation (always true):

$$S(E) = -k_B \sum_{i}^{\text{all states}} P_i \ln P_i \tag{22}$$

Boltzmann ratio (Schroeder 6.1)

$$\frac{P_i}{P_j} = e^{-\frac{E_i - E_j}{k_B T}} \tag{23}$$

$$P_i = \frac{e^{-\frac{E_i}{k_B T}}}{Z} \tag{24}$$

$$Z = \sum_{j}^{\text{all states}} e^{-\frac{E_j}{k_B T}} \tag{25}$$

Thermal averages (Schroeder 6.2) The average value of any quantity is given by the weighted average

$$\langle X \rangle = \sum_{i}^{\text{all states}} P_i X_i \tag{26}$$

In particular, the internal energy is given by

$$U = \sum_{i}^{\text{all states}} P_i E_i \tag{27}$$

Helmholtz free energy from statistics

$$F = -kT \ln Z \tag{28}$$