Corrections

6. 300 K   29 g/mol

B. diffusion coefficient, 300 K

4. $\left(\frac{\partial P}{\partial G}\right)_T = \left(\frac{\partial P}{\partial T}\right)_G =$

CHMY 361

Final Exam

Name __KEY_____

Last,   First

***(200 points) Be sure you have 10 problems on 6 pages** including Tables A1 and A5.*

Read: **In this exam, there should be time to avoid nonsensical answers. Most of the answers can be estimated without doing any arithmetic. If you get a quantitative answer which is very far from what you think it should be and cannot find the error, you will be rewarded for pointing out approximately what you expected and why. You will be penalized by 25% on a problem for sign and unit errors that lead to unreasonable results if you do not say why it is unreasonable.**

For full credit show all work and put correct units on final answers.

(25 pts) **1.** Consider the following: Within the boundaries that you have defined as System, you observe that a mass of 100 kg is raised 3 meters against the force of Earth's gravity (g=9.8 ms^{-2}) and the temperature decreases by 1 K. You also know the heat capacity of the System is 10 J/K. You have not made any measurements outside the system. Answer the following questions. If there is not enough information to answer any of them, tell what you would need to know in order to answer them.

(a) What is ΔU? $\Delta U = mgh + C\Delta T$

$= 100\,kg \; 9.8\,m\,s^{-2} \times 3m \; - \; 10\,\frac{J}{K} \times 1K$

$= \boxed{2930\ J}$

(b) What are q and w?

q & w cannot be known without measurements in the surroundings

q: must see a temperature change in an object with known heat capacity in surr.

W: must observe a measurable mechanical energy change in surr,

(all we know is q + w = ΔU = 2930 J)

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(25 pts) 2. A system initially containing water and crystals of an unknown salt eventually comes to an equilibrium state in which all of the crystals have dissolved. The process is carried out isothermally with constant atmospheric external pressure. The pressure of the system is equal to the external pressure, (meaning that the system can expand or contract) and it was necessary to cool the surrounding during the process in order to maintain constant temperature. The partial molar volume of the dissolved salt is larger than the molar volume of the crystals. The only work involved is due to volume change against the external pressure, i.e., no useful work done or used.

Tell whether the following are positive, zero, or negative with the symbols **+, -, 0, or ?**, where the **?** means it is not possible to determine anything definite. *Give a brief justification for each of your answers.*

$$q\ \underline{-}\quad w\ \underline{-}\quad \Delta T\ \underline{0}\quad \Delta U\ \underline{-}\quad \Delta H\ \underline{-}\quad \Delta S\ \underline{?}\quad \Delta G\ \underline{-}\quad \Delta S_{surr}\ \underline{+}\quad \Delta S_{univ}\ \underline{+}$$

$\Delta S_{UNIV} = +$ it happened

$\Delta S_{surr} = -q/T = +$

$\Delta H = \Delta U + \Delta PV = \Delta U + P\Delta V^{+} = q$ under these conditions = negative

$\Delta G = -T\Delta S_{UNIV} + W_{other}^{=0} = -T\Delta S_{UNIV} = $ negative

$\Delta G = \Delta H - T\Delta S$
  $\underline{-}$ $\uparrow$
           $+$ or $-$ ΔS could be negative as long
                  as $\Delta S + \Delta S_{surr} = +$

(20 pts)   3. In a typical "lithium battery", lithium atoms are intercalated within a cobalt oxide crystal lattice. The discharging of this battery has $\Delta G = -300{,}000$ J/mol in which Li → $Li^+(aq) + e^-$ is the source of voltage and current to run cell phones and laptops.
The charging of this battery is the reverse reaction and has $\Delta G = +300{,}000$ J/mol, yet is a spontaneous process.

Using the Second Law of Thermodynamics, explain how a process with positive ΔG can be spontaneous.

$$\Delta G = -T\Delta S_{univ} + W_{other}.$$
              $\uparrow$
              $+$

$-T\Delta S_{univ}$ will be negative in a spontaneous process but input of W_{other} that is large and positive will be consistent with $\Delta G = +$

(20 pts) 4. (a) Define Gibbs energy, G.

$$G = H - TS$$

(b) Given that dG = Vdp − SdT one may write
dp =(1/V) dG + (S/V)dT

$$\left(\frac{\partial p}{\partial G}\right)_T = \frac{1}{V}$$

$$\left(\frac{\partial p}{\partial T}\right)_G = \frac{S}{V}$$

$$\left(\frac{\partial \frac{1}{V}}{\partial T}\right)_G = \left(\frac{\partial \frac{S}{V}}{\partial G}\right)_T$$

(20 pts) 5. Using the concept of vapor pressure and boiling point in a knowledgeable and accurate manner, describe what happens and why it happens as one raises the temperature of a beaker of water from just below the boiling point to just above the boiling point if:

(a) there are absolutely no gas bubbles in the water.

Nothing* will happen. Water will become super heated

* Of course, water is evaporating from the surface at all temperatures. If the water ~~should~~ at any time while ~~it is~~ super-heated receive a "bubble" (~~this~~ might be a flake of dust or hair) violent boiling will immediately start.

(b) there are gas bubbles in the water.

evaporation into bubbles will begin to expand bubbles just above the boiling point i.e. boiling.

Again, boiling is evaporation into bubbles. When above the boiling point, evaporation causes any bubble to grow until it breaks away from the glass and rises to surface. But, it always leaves behind a small bubble[3], which grows & rises to the surface . . . .

(20 pts) **6.** Using the Boltzmann distribution equation, calculate the atmospheric pressure in Bozeman (1720 m above sea level). at 300 K. molar mass of air = $29\,g/mol$

$$\frac{P_2}{P_1} = e^{-\frac{mgh}{kT}} = e^{-\frac{Mgh}{RT}} = \frac{P_{Boze}}{1} \quad e^{-\frac{0.029 \cdot 9.8 \cdot 1720}{8.3145 \cdot 300}}$$

$$= e^{-0.19} = \boxed{0.82 \text{ atm or bar}}$$

(20 pts) **7.** If d(humans)/dt = k × number of humans = 1.33×10^8 humans/year, and the current number is 7 billion (7×10^9):

(a) What is the rate constant, k, in year^{-1}?

$$\frac{d \text{ humans}}{dt} = 1.33 \times 10^8 \text{ humans yr}^{-1} = K \times 7 \times 10^9$$

$$K = \frac{1.33 \times 10^8}{7 \times 10^9} = 0.019 \text{ year}^{-1}$$

(b) How long until the population has increased to 10 times that much?

$$10 = e^{+K t_{10}} =$$

$$\ln 10 = K t_{10}$$

$$\frac{\ln 10}{K} = t_{10} = \frac{2.303}{0.019 \text{ year}} = \boxed{121 \text{ years}}$$

(c) If the birthrate decreased and mortality rate increased such that the population decreased by 1.33×10^8 humans/year how long would it take for the population to decrease to 1/10 of its present value?

$$\frac{1}{10} = e^{-Kt} =$$

$$10 = e^{+Kt} \quad \text{therefore SAME ANSWER}$$

$$= \boxed{121 \text{ years}}$$

121

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at 300 K

(20 pts) 8. If an object with mass of a typical protein = 1 x 10^{-21} kg has a terminal velocity of 1 cm/hour when a force of 1 x 10^{-15} newtons is applied, what is its ~~diffusion constant~~? coefficient

$$U_{term} = \frac{Force}{Frictional\ Coef} = \frac{1\times10^{-15}\ kg\,m\,s^{-2}}{f} = \frac{1\,cm}{hr} \times \frac{0.01\,m}{3600\,s}$$

$$U_{term} = 2.78\times10^{-6}\ m\,s^{-1}$$

$$f = \frac{force}{U_{term}} = \frac{1\times10^{-15}\,kg\,m\,s^{-2}}{2.78\times10^{-6}\,m\,s^{-1}} = \boxed{f = 3.6\times10^{-10}\ kg\,s^{-1}}$$

$$D = \frac{K_B T}{f} = \frac{(1.38\times10^{-23})(300)\ kg\,m^2\,s^{-2}\,K^{-1}\,K}{3.6\times10^{-10}\ kg\,s^{-1}} = \boxed{1.15\times10^{-11}\ \frac{m^2}{s}}$$

(20 pts) 9. Write the wavelength, or frequency, or wavenumber in cm^{-1} corresponding to the following types electromagnetic radiation, and describe the *minimum* energetic action it causes.

a. radio waves $600\times10^6\ s^{-1}$ flips nuclear spins

b. x-rays $\sim 1\ A^\circ$ ionize (eject electrons)

c. microwaves $0.01\ cm^{-1}$ increase rotational energy

d. visible light   excite electrons (and photochemistry.) $400 - 700\ nm$

e. UV light   " " (and photochemistry) $100 - 400\ nm$

f. infrared light   excite vibrations $200 - 4000\ cm^{-1}$

(10 pts) 10. Diffraction of molecules with molar mass = 0.1 kg/mol = 1.66 x 10^{-25} kg/molecule traveling 500 ms^{-1} i.e., momentum = 8.33 x 10^{-23} kgms^{-1} has been reported.

What is the wavelength of such a particle in nm?

$$\lambda = \frac{h}{P} = \frac{6.62\times10^{-34}\ (kg\,m^2\,s^{-2})\,s}{8.33\times10^{-23}\ kg\,m\,s^{-1}} \quad \leftarrow Js$$

$$= 7.95\times10^{-12}\ m = \boxed{7.95\times10^{-3}\ nm}$$

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Constant	Symbol	SI units	cgs-esu units
Gas constant	R	8.3145 J K^{-1} mol^{-1}	8.3145×10^7 erg deg^{-1} mol^{-1} 1.987 cal deg^{-1} mol^{-1} 0.08205 L atm deg^{-1} mol^{-1}
Avogadro's number	N_0	6.0221×10^{23} mol^{-1}	6.0221×10^{23} molecules mol^{-1}
Boltzmann constant	k	1.3807×10^{-23} J K^{-1}	1.3807×10^{-16} erg deg^{-1}
Faraday constant	f	9.6485×10^4 C mol^{-1}	9.6485×10^4 C mol^{-1}
Speed of light	c	2.9979×10^8 m s^{-1}	2.9979×10^{10} cm s^{-1}
Planck constant	h	6.6261×10^{-34} J s	6.6261×10^{-27} erg s
Elementary charge	e	1.6022×10^{-19} C	4.8030×10^{-10} esu
Electron mass	m_r	9.1094×10^{-31} kg	9.1094×10^{-28} g
Proton mass	m_p	1.6726×10^{-27} kg	1.6726×10^{-24} g
Standard gravity	g	9.8066 m s^{-2}	980.66 cm s^{-2}
Permittivity of vacuum	ε_0	8.8542×10^{-12} C^2 N^{-1} m^{-2}	

C = coulomb   L = liter
g = gram   m = meter
j = joule   N = newton
K = Kelvin   s = second
kg = kilogram

TABLE A.5 Inorganic Compounds*

	$\Delta H_f^0 \equiv \bar{H}^0$ (kJ mol^{-1})	$\bar{S}^0$ (J K^{-1} mol^{-1})	$\Delta G_f^0 \equiv \bar{G}^0$ (kJ mol^{-1})
Ag(s)	0	42.55	0
Ag$^-$(aq)†	105.579	72.68	77.107
AgCl(s)	−127.068	96.2	−109.789
C(g)	716.682	158.096	671.257
C(s, graphite)	0	5.740	0
C(s, diamond)	1.895	2.377	2.900
Ca(s)	0	41.42	0
CaCO$_3$(s, calcite)	−1206.92	92.9	−1128.79
Cl$_2$(g)	0	223.066	0
Cl$^-$(aq)	−167.159	56.5	−131.228
CO(g)	−110.525	197.674	−137.168
CO$_2$(g)	−393.509	213.74	−394.359
CO$_2$(aq)	−413.80	117.6	−385.98
HCO$_3^-$(aq)	−691.99	91.2	−586.77
CO$_3^{2-}$(aq)	−677.14	−56.9	−527.81
Fe(s)	0	27.28	0
Fe$_2$O$_3$(s)	−824.2	87.40	−742.2
H$_2$(g)	0	130.684	0
H$_2$O(g)	−241.818	188.825	−228.572
H$_2$O(l)	−285.830	69.91	−237.129
H$^+$(aq)	0	0	0
OH$^-$(aq)	−229.994	−10.75	−157.244
H$_2$O$_2$(aq)	−191.17	143.9	−134.03
H$_2$S(g)	−20.63	205.79	−33.56
N$_2$(g)	0	191.61	0
NH$_3$(g)	−46.11	192.45	−16.45
NH$_3$(aq)	−80.29	111.3	−26.50
NH$_4^+$(aq)	−132.51	113.4$^-$	−79.31
NO(g)	90.25	210.761	86.55
NO$_2$(g)	33.18	240.06	51.31
NO$_3^-$(aq)	−205.0	146.4	−108.74
Na$^+$(aq)	−240.12	59.0	−261.905
NaCl(s)	−411.153	72.13	−384.138
NaCl(aq)	−407.27	115.5	−393.133
NaOH(s)	−425.609	64.455	−379.494
O$_2$(g)	0	205.138	0
O$_3$(g)	142.7	238.93	163.2
S(rhombic)	0	31.80	0
SO$_2$(g)	−296.830	248.22	−300.194
SO$_3$(g)	−395.72	256.76	−371.06

* Standard thermodynamic values at 25°C (298 K) and 1 atm pressure. Values for ions refer to an aqueous solution at unit activity on the molarity scale. Standard enthalpy of formation, ΔH_f^0, third-law entropies, S^0, and standard Gibbs free energy of formation, $\Delta G_f^{\bullet}$, are given.

† The standard state for all ions and for species labeled (aq) is that of a solute on the molarity scale.

SOURCE: Data from *The NBS Tables of Thermodynamic Properties*, D. D. Wagman et al., eds., *J. Phys. Chem. Ref. Data*, 11, Suppl. 2 (1982).