Chem 155 **First Hour Examination** **October 9, 2002**

Name:_____

Full credit will be given to correct answers only when all necessary steps are shown

(12) 1. True of false? Just write "T" or "F" after each question.

(a) $\left(\frac{\partial K_P}{\partial P}\right)_T = 0$ for an ideal gas reaction T

(b) The entropy of all substances is zero at 0 K. F

(c) ΔG is a state function. F

(d) $\Delta U = 0$ for any isothermal process in a closed system. F

(e) In a spontaneous process, the change of entropy of the system is always positive. F

(f) The temperature of an ideal gas remains constant when it expands against a vacuum. T

(12) 2. List the condition(s) under which each of the following equations can be applied. If no conditions are required, write "none."

(a) $dG \leq 0$ for equilibrium and spontaneity

constant T and P

(b) $\Delta G = \Delta H - \Delta(TS)$

None

(c) $w = -P\Delta V$

Irreversible expansion or compression

(d) $\Delta S = nR\ln\frac{V_2}{V_1}$

Isothermal, ideal gas

(e) $w = C_v(T_2 - T_1)$

C_v independent of T, adiabatic

(f) $\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$

ΔH° and ΔS° independent of T

(4) 3. When a bicycle tire is pumped with a hand-pump, the temperature of the air in the tire rises. Give a brief thermodynamic analysis for this observation. (*Hint*: The pumpimg action is usually fast so the process can be assumed to occur adiabatically.)

$\Delta U = q + w \qquad q = 0$

$\Delta U = w$

Work done on the system so $w > 0$ and $\Delta U > 0$.

The average KE of the gas increases, so T increases

(4) 4. Which of the following compounds has the largest $\overline{C}_v$ value at 298 K? Provide a one sentence explanation.

Ne CH_4 H_2

CH_4 because it is a polyatomic molecule and therefore has more molecular motions (rotation and vibration) to store energy.

(8) 5. Supersaturated solutions are thermodynamically unstable. On standing, crystals appear spontaneously from a supersaturated solution of sodium acetate. Based on this information, conclude whether the process is endothermic or exothermic.

Spontaneous: $\Delta G < 0$

Crystallization: $\Delta S < 0$

$\Delta G = \Delta H - T\Delta S$

$\Delta H = \Delta G + T\Delta S < 0$

The process is exothermic.

(4) 6. A quantity of 1,00 mole water vapor initially at 350°C and 1.00 atm undergoes a cyclic process for which q = –84 J. Calculate ΔS for the process.

$\Delta S = 0$ for a cyclic process because S is a state function.

(4) 7. Which of the following standard molar enthalpies of formation is not zero at 25°C? Just circle your answer.

Na(*s*) Hg(*l*) (Br$_2$(*s*)) He(*g*) Cl_2(*g*) Mg(*s*)

(8) 8. Show with proper equations that, for an ideal gas, $\left(\frac{\partial H}{\partial P}\right)_T = 0$.

$H = U + PV$

$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T$

$\left(\frac{\partial U}{\partial P}\right)_T = 0$ (just like $\left(\frac{\partial U}{\partial V}\right)_T = 0$) for an ideal gas.

Also, PV = constant at constant T (Boyle's law).

Therefore, $\left(\frac{\partial (PV)}{\partial P}\right)_T = 0$ and $\left(\frac{\partial H}{\partial P}\right)_T = 0$

(16) 9. For each of the following processes deduce whether each of the quantities of the system listed below is positive (+), negative (–), or zero.

(a) Freezing benzene at 1 atm and its normal freezing point.

(b) Adiabatic compression of an ideal gas.

(c) Cooling of an ideal gas at constant volume.

(d) Subliming dry ice (solid CO_2) at room temperature.

	q	w	ΔU	ΔH
(a)	–	+	–	–
(b)	0	+	+	+
(c)	–	0	–	–
(d)	+	–	+	+

(10) 10. At 25°C, the equilibrium pressure of O_2 from the decomposition of a hypothetical metal oxide MO to M_2O and O_2 is 0.049 bar:

$$4MO(s) \rightleftharpoons 2M_2O(s) + O_2(g)$$

Calculate $\Delta_f \overline{G}^\circ$ for M_2O, given that $\Delta_f \overline{G}^\circ$ for MO is –127.2 kJ mol^{-1}.

$\Delta G^\circ = -RT \ln K_p$

$K_p = P_{O_2}$ (solids do not appear in the equilibrium constant expression)

$= 0.049$

$\Delta G^\circ = -(8.314\ J K^{-1} mol^{-1})(298\ K) \ln 0.049$

$= 7.47 \times 10^3\ J\ mol^{-1}$

$= 7.47\ kJ\ mol^{-1}$

$\Delta G^\circ = (2)\Delta_f \overline{G}^\circ(M_2O) + (1)\Delta_f \overline{G}^\circ(O_2) - (4)\Delta_f \overline{G}^\circ(MO)$

$7.47\ kJ\ mol^{-1} = (2)\Delta_f \overline{G}^\circ(M_2O) + 0 - (4)(-127.2\ kJ\ mol^{-1})$

$\Delta_f \overline{G}^\circ(M_2O) = -251\ kJ\ mol^{-1}$

(12) 11. A quantity of 3.0 moles of an ideal gas undergoes an isothermal, reversible compression from 2.0 L to 1.0 L at 20°C.

(a) Calculate w, q, ΔU, ΔH, ΔS, and ΔG for the process.

$$w = -nRT \ln \frac{V_2}{V_1} = -(3)(8.314)(293) \ln \frac{1.0}{2.0} = +5.07\ kJ$$

$$q = -w = -5.07\ kJ$$

$\Delta U = 0$ Ideal gas, isothermal

$\Delta H = 0$ Ideal gas, isothermal

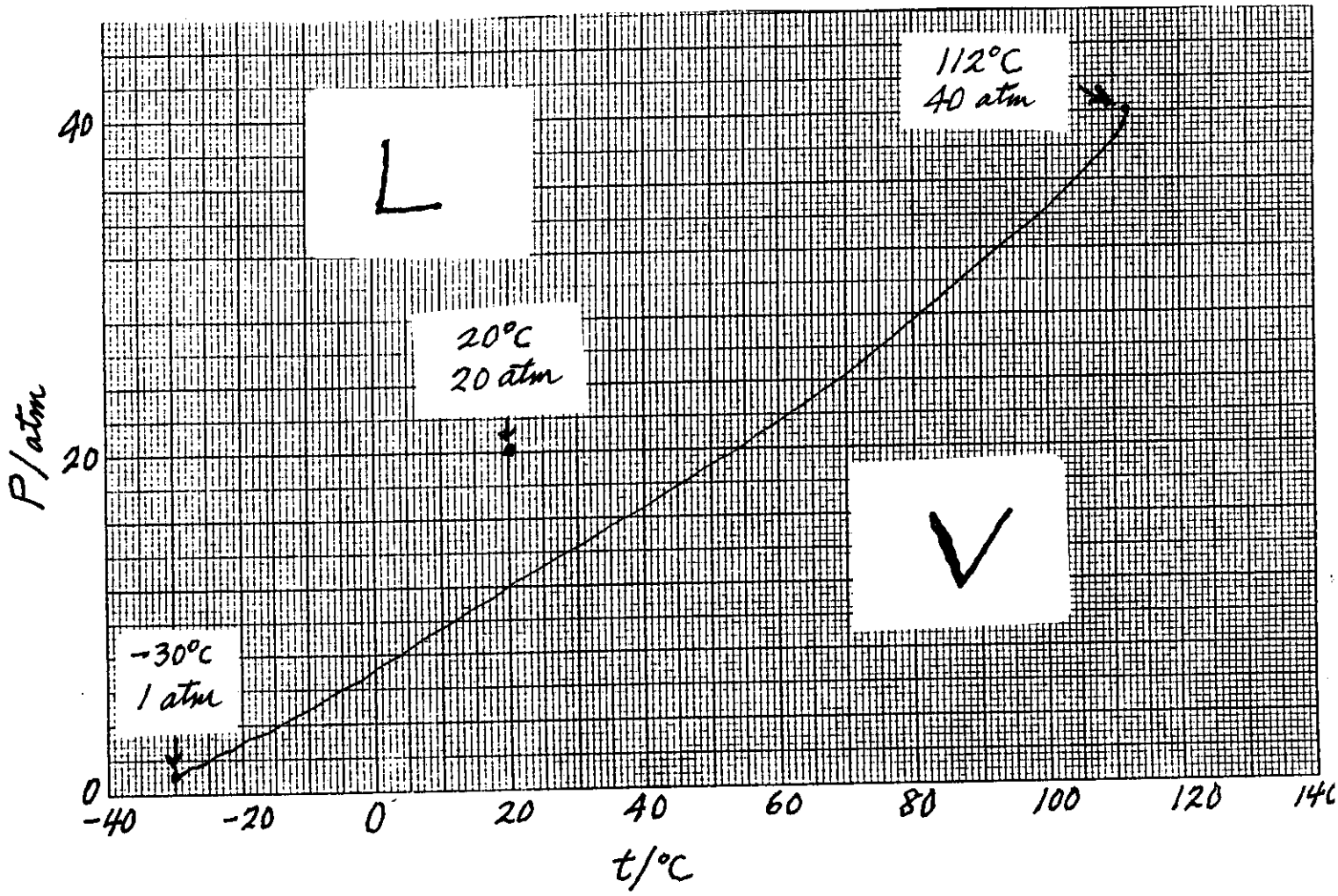
$$\Delta S = nR \ln \frac{V_2}{V_1} = (3)(8.314) \ln \frac{1.0}{2.0} = -17.3\ J\,K^{-1}$$

$$\Delta G = \Delta H - T\Delta S$$
$$= 0 - (293\ K)(-17.3\ J\,K^{-1})$$
$$= 5.07\ kJ$$

(b) Explain whether this process represents maximum work done on the gas. If not, what does it represent?

In a reversible compression, the work done is the minimum work that can be done because the opposing pressure is kept at a minimum at every stage of compression.

(6) 12. A chlorofluorocarbon, called dichlorodifluoromethane (CCl_2F_2), has a normal boiling point of –30°C, a critical temperature of 112°C, and a corresponding critial pressure of 40 atm. If CCl_2F_2 gas is compressed to 20 atm at a temperature of 20°C, will the gas liquefy? Your answer should be based on a graphical interpretation.



Because 20°C/20 atm combination lands in the L (liquid region), the gas will liquefy.

I have neither received nor given aid on this examination: _____